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RECLAMATION OF METAL VALUES FROM METAL-FINISHING WASTE TREATMENT SLUDGES

Arch B. Tripler, Jr., et al

Battelle Columbus Laboratories

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RECLAMATION OF METAL VALUES FROM METAL-FINISHING WASTE TREATMENT SLUDGES

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

As part of these activities, efforts of this study have included the determination of the worth of recovering metal values from metal finishers' wastewater treatment sludges, the definition and research of processes for such recovery, and the selection, design, and costing of a recommended process.

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ABSTRACT

The efforts of this program have included the determination of the worth of recovering metal values from metal finisher's wastewater treatment sludges, the definition and research of processes for such recovery, and the selection, design, and costing of a recommended process.

The study included a survey of the literature to determine the state of the art regarding the generation, disposal, and recovery treatment practices relevant to metal-finishers' sludges, and to identify metal recovery processes possibly applicable to those sludges. This information was supplemented with a survey by questionnaire to determine the current status of relevant practices and conditions.

Field investigations provided detailed examples of plant practices, sludge storage conditions, and sludge characteristics such as water content and chemical composition. Further, a detailed study was performed to determine, for one lagoon, the degree of leaching of metals from the sludge into the underlying soil structure. Samples of sludge were obtained from operating plants for use in the experimental program.

The extraction of metal values from waste sludges by various leaching agents, and the recovery of metal values by techniques including electrowinning, cementation, and liquid-liquid ion exchange were studied on a bench scale during the program.

On the basis of the information developed in the prior portions of the program, a portable pilot process for the treatment of waste sludges and recovery of metal values was selected and equipment and operating costs developed.

This report was prepared by Battelle for the Metal Finishers' Foundation and was sponsored by Grant No. 12010 FXD with the U. S. Environmental Protection Agency.

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SECTION I

CONCLUSIONS

On the basis of information gathered in the literature survey, it is concluded that the metal-finishing industry in the United States rarely treats sludges to recover plating metals, either for economic gain or for further detoxification of the sludge. This finding is borne out by the results of the plant survey by questionnaire.

The quantity, distribution, and physical and chemical properties of metal-finishing sludges are believed to account for this lack of activity in metal recovery and further detoxification.

There are undoubtedly some specific instances, none of which came to light in this study, where sludges could be profitably worked for metal recovery and detoxification. Such instances would have to be uncovered and evaluated by pointed studies. It must be emphasized that, in general, there is no discrete "sludge treatment" process available.

Two general approaches to the recovery of metals and the detoxification of sludges, which were investigated in a preliminary manner in this study, are believed to be the most promising routes to follow in the design and development of a given metal-finishing sludge treatment process. There are:

(a) Sulfuric acid dissolution to dissolve metal hydroxides and precipitate calcium sulfate, followed by filtration to obtain a clear pregnant liquor.

(b) Solution in ammonia-ammonium carbonate solution followed by filtration to produce a pregnant liquor.

The details of recovery processes based on these two approaches could be settled upon only after full information was available on the quantity and composition of a sludge under consideration.

On the basis of data developed during this study, it would be uneconomic to apply the sulfuric acid leaching approach to mixed sludges (containing nickel, copper, and chromium) of typical composition (3 to 5% Ni, 3 to 5% Cu, 5 to 15% Cr, on a dry solids basis) unless the process could be carried out on a large, and preferably continuous scale.

Preliminary cost estimates on a small batch operation capable of handling only 100 lb per day of dried sludge indicated a daily operating cost of about $85.00 with but a few dollars realizable from recovered metals. It is estimated that the minimal feed rate would have to be in the range of 2,000 to 5,000 lb of sludge (dry basis) solids per day even with a thoroughly developed process.

Although no economic studies were made on the ammonium carbonate leaching approach, it is judged that this type of process would be applicable only on an even larger scale, owing to the cost of reagent and the necessity for incorporating ammonia recovery system in the plant.

In the design of any process based on either of these two approaches, electrolysis or electrowinning of such metals as copper, nickel, and cadmium should receive prime consideration, because its tools and technology are shared with metal-finishing. The laboratory work demonstrated the general feasibility of this approach.

Chromium and zinc in mixed metal-finishing sludges are dubious assets, if not liabilities, because of their low unit price and the complications they can introduce to chemical processing. The technical and economic feasibility of treating segregated sludges with chromium and zinc as single base-metal components would have to be judged on a case-by-case basis.

Although no work was done to examine the feasibility of recovering tin and procious metal reported in some of these slugdes, their extraction and recovery would require additional and possibly exotic processes.

Liquid ion exchange as a process for separating metals in mixed sludges was examined at length in this study. It does not appear to offer much hope as an economic approach to the problem.

In the single case investigated in this study, it was determined by a core-drilling and analytical program that a sludge lagoon in service about 12 years had not contaminated ground water underlying the lagoon bed.

It was proposed originally that fluidized-bed drying and/or calcination might be an attractive route for dewatering the sludges so that they could be shipped a reasonable distance to a centralized recovery plant. Following the survey of plating plants, it was concluded that this approach generally would not be feasible. The data indicated that the quantities of sludge produced at most individual plant sites were too small to warrant the expense of installing and operating a fluidized-bed

system. For those areas in which a relatively heavy concentration of plating plants exists, the installation of a centrally-located wet processing facility to process filtered sludge is believed to be more practical.

SECTION II

RECOMMENDATIONS

In general, the recovery of metals by treating mixed sludges that currently are being produced by metal-finishing plants or that have been stored by chemical processes is not economically attractive. This is because most such sludges are too low in grade in metal values, are complex mixtures that require difficult and expensive separations, and are variable in quantity, composition, and consistency. However, increasing environmental restrictions may preclude the use of the landfill option in some areas and make other techniques, e.g., segregation of waste streams and metal recovery, necessary.

Currently, the only practical way to treat most mixed metal-finishing sludges now being produced is to landfill them, preferably after dewatering and/or solidification.

There may be a few instances in the metal-finishing industry where the quantity and grade of the sludges being produced or those stored may be great enough to warrant complex chemical processing at a centralized treatment facility. A separate study aimed at uncovering such instances should be made. The specific aims of this study should parallel those of the mining prospector and developer: (1) to locate likely sites (such as large sludge deposits at a single facility or clusters of sludge deposits from a number of facilities within which a centrally located treatment plant might be established, (2) to determine the quantity and grade of sludge available for treatment in the given area, (3) to devise a process that could be applied to the treatment of such sludges, and (4) to work out preliminary economic estimates on the processes.

Metal finishers should be encouraged to keep sludges from various plating lines separate to enhance the possibility that simple, straightforward, and hence, inexpensive, recovery processes might be used. Advantageous metal associations would be copper alone, nickel alone, cadmium alone, tin alone, precious metals alone, copper plus nickel, copper plus nickel plus precious metals. Chromium should, where possible, be kept out of mixed sludges because in the form in which it is readily recoverable, it has little value because it complicates and adds expense to separation processes, and because when eventually separated, its ultimate destination would very probably still be a landfill. Similarly, zinc, where possible, should be excluded from mixed sludges, even cadmium sludges, because it, too, is a low value material that complicates chemical separations.

If segregation of metal values in sludges can be achieved, the opportunities for metal recovery probably would increase enormously, even for metals like chromium and zinc. In such cases, simple filtering/drying could conceivably produce a product that the plater could store in a low volume and dispose of to refineries or centrally located disposal plants. It is recommended that the problem of sludge disposal and detoxification be reexamined from the specific viewpoint of what could be done if proper segregation of plating sludges were practiced. A study of this nature would involve an assessment of foreign practice (England, Japan, etc.) where some form of segregation and recovery is practiced. It also would include a survey of sludge production in the U.S. to determine the major areas in which sludges are produced and the nature of these materials. The overall objective would be to determine the feasibility of centralized processing facilities for treating segregated sludges.

SECTION III

INTRODUCTION

Many of the potential hazards accompanying the unrestricted disposal of wastes from biological and industrial processes have been recognized for several hundred years. Only in recent years, however, have the complexity and intensity of the problems involved in waste management and disposal reached the point where the quality of the air-land-water environment is critically impaired in many geographical areas. Increasingly restrictive legislation has been passed as efforts to curb pollution have been intensified.

Industrial wastes have contributed heavily to the degradation of the quality of man's environment and many industries have invested considerable sums of money in efforts to abate pollution. The nature of the waterborne wastes produced in metal-finishing operations is such that complex and costly methods have been needed to prevent the contamination of water supplies with the compounds used by this segment of the industrial world.

The specific steps involved in the treatment of these wastes vary considerably from installation to installation. However, the general treatment consists of: (1) separation of grease and oil; (2) reduction of chromates; (3) oxidative destruction of cyanides; (4) neutralization and liquid-solid separation; and (5) disposal of the sludge. The metals initially present in the wastewaters are precipitated as hydroxides during treatment operation number (4).

The metal-bearing sludges are difficult to handle and their final disposal often is the most troublesome and costly aspect of the treatment of metal-finishing wastes. Increasing congestion of urban areas in which many of the larger plating facilities are located together with the accompanying increases in the cost of land add to the problems involved in ultimate disposal. The finely divided precipitates contained in these sludges are a potential source for pollution of surface and ground waters.

In addition to the problem of handling and disposal of these sludges, they contain large quantities of relatively valuable metals--copper, nickel, chromium, cadmium, etc.--which often are in short supply. The value of the nickel and chromium lost in plating wastes in the United States has been estimated at 25 to 30 million dollars per year. Sludges selected from various steps in the waste treatment procedure may contain 10 to 15 percent of nickel, chromium, etc., on a dry basis--

concentrations greater than those found in most ores containing these metals. The extraction and recovery of the more valuable metals from the sludges should ideally involve relatively simple techniques. The economic feasibility of recovery would be largely dependent on the size of the plating facility, the cost of the primary raw materials used in the plating operations, and the cost of alternative methods of sludge disposal, e.g., lagoons, landfills, etc.

Because of the importance of eliminating potential water pollution problems, conserving natural resources, and recovering valuable materials, an investigation was undertaken of the possible recovery of metals from sludges produced during the treatment of metal-finishing wastes. Because this is a general problem in the metal-finishing industry, the investigation was supported by a grant from the U. S. Environmental Protection Agency to the Metal Finishers' Foundation. This allowed Battelle to work closely with an important segment of the industry in seeking a solution to this problem. The National Association of Metal Finishers has approximately 100 members who have waste treatment facilities in which sludges are produced.

SECTION IV

BACKGROUND INFORMATION

There are between 15 and 20 thousand metal-finishing facilities in the United States. These include several thousand small shops, a number of large independent shops and many captive metal finishing facilities associated with industries such as automobiles, aircraft, and home appliances. Although the composition and volume of the wastewaters from these shops vary considerably from plant to plant, they include in general the following:

(1) Rinse waters from plating, cleaning, and other surface finishing operations.

(2) Concentrated plating and finishing baths that are intentionally or accidentally discharged.

(3) Wastes from plant or equipment cleanup.

(4) Sludges, filter cakes, etc., produced by naturally occurring deposition in operating baths or by intentional precipitation in the purification of operating baths, chemical rinsing circuits, etc., when flushed down sewers.

(5) Regenerants from ion exchange units.

(6) Vent scrubber waters.

The volumes as well as the compositions of the sludges produced in the treatment of metal-finishing waste effluents are widely varied. Among the variables which influence the volume and composition are: (1) the characteristics of the finishing effluent treated, and (2) the treatment method employed.

Although some companies have considered the recovery of metals from metal-finishing waste sludges, the additional processing required generally has not been considered seriously because of the relative simplicity of current disposal methods and the lack of economic incentive. Increasing restrictions governing the disposal of solid wastes together with the increasing cost of land in urban areas for disposal purposes are among the factors which make a study of additional processing of sludges of this nature desirable. In addition to advantages which may accrue from effecting reduced volumes of sludges by

further processing, the potential recovery of valuable metals and the reduced cost of transporting the sludges to disposal sites are further incentives for the consideration of such treatment. Some of the larger metal-finishing installations each year discard sludges containing metals valued at $150,000 to $200,000 and often pay in excess of $50,000 for hauling these sludges to disposal sites. If a simple, technically feasible technique can be developed to recover the more valuable metals and to effect a substantial reduction in the volume of sludge to be transported, the value of the metals recovered and the anticipated reduction in hauling costs may be more than sufficient to offset the additional processing costs. This would provide an economic incentive for such processing which, in turn, would help to alleviate the problem of sludge disposal and pollution of valuable land areas with solid wastes.

SECTION V

OBJECTIVES OF THE RESEARCH PROGRAM

Battelle's preliminary surveys had indicated that the removal of metals from sludges may simplify their disposal and diminish their potential for pollution by leaching into ground and surface waters. These surveys also suggested that the reclamation of valuable metals (nickel, copper, cadmium, etc.) from sludges produced in waste-treatment plants might significantly reduce the net cost of sludge disposal.

This study was made in some depth to evaluate these possibilities. Specific objectives of the study were:

(1) To acquire further information on the quantity and chemical and physical characteristics of metal finishing sludges being produced in the United States by plants of various sizes and types;

(2) To investigate and evaluate techniques that might be applicable to the treatment of metal finishing sludges and to the recovery of metal values from them, basing the investigative and evaluative work on information gathered from the literature plant surveys;

(3) To conduct bench-scale laboratory work on actual sludges using specific approaches suggested by the literature studies, or other considerations, to have the most promise;

(4) To make preliminary economic estimates of the capital and operating costs that might be encountered in such treatment and/or recovery processes;

(5) To investigate on a necessarily limited scale, the effects of weathering on stored sludge beds, to provide some data as to the permeability of leachates from these beds into ground water;

(6) To formulate specific recommendations based on the findings of this study, as to the direction that future work on the sludge disposal and treatment problem should take.

SECTION VI

ACQUISITION OF EXISTING INFORMATION

Literature Review

The literature search performed as part of this program served to gather information relative to all phases of the work, including both industrial practices and trends, the state of the art in electroplater's sludge generation, disposal, and recovery processes, and technical details of the unit processes selected for experimental use. An extensive literature review is given in Appendix A of this report, providing more detailed descriptions of the content of various published references and guidance for any subsequent follow up to this work.

In summary, the literature survey established the following bases or trends relevant to this study:

(1) That, currently, in the United States, only a few instances of metal recovery from metal finishing wastes are being applied on a routine, commercial-scale basis.

(2) That the practices of recovery of metal values from such wastes is slightly more advanced in England than in the United States, and that, there, the economics of recovery processes are dictating a trend toward segregation of waste streams to produce single-metal treatment sludges.

(3) That access to lagoon storage and landfill disposal is decreasing due to factors of decreased availability of space or more stringent anti-pollution regulations.

On the basis of the literature survey, observations relating to metal-recovery processes included the following:

(1) That current metal reclamation processes are tailored to specific plants and generally reclaim only one metal.

(2) That the few instances of the practice of sludge dewatering (by vacuum-filtration, natural evaporation, or incineration) are applied principally to achieve decreased sludge volumes, i.e., to extend storage capacity. Concurrent oxidation during incineration destroys or stabilizes cyanides but solubilizes chromium.

(3) That the unit processes currently applied or studied for recovery of metal values include:

(a) cementation (to recover copper)
(b) a portable copper electrowinning unit
(c) electrowinning of zinc (with variable success)
(d) electrolytic regeneration of chromic acid
(e) constant cathode potential electrolytic recovery of copper or nickel
(f) precipitation of iron or nickel as hydroxides.

The balance of the literature reviewed in Appendix A contributed details of these major points or were consulted for specifics of experimental process conditions.

Survey of Plants

Six hundred and sixty-six questionnaires (see Appendix B, "Details of Plant Survey - Questionnaire") were mailed to members of the NAMF, including a few foreign members. One hundred and fifty replies were received for a percentage of 22.5. This is considered an average response. In some cases the respondents did not return a filled-in questionnaire but, instead, wrote letters explaining their special position in the metal-finishing field. Each of these letters was counted as a response even though in most of these cases not all of the desired information was given.

As shown in Table 1, slightly more than one-half the respondents are collecting various amounts of waste slude (Item 1). Slightly less than half of those companies accumulating sludge (about 25 percent of the total number responding) employ a special treatment operation to

precipitate the sludge (Item 2). The others who accumulate sludge do so as a result of what might be termsed "accidental" neutralization where alkaline and acid wastewaters are mixed (Item 3). Fifty of the respondents (33 percent) who do not now have treatment facilities are planning installations in the near future (Item 4). Probably others will be following because 103 respondents (69 percent) reported activity on the part of various governmental authorities (Item 5).

Sizable amounts of sludge appear to be available for the reclamation of metal values. An extrapolation of the information obtained suggests that the 666 members of NFF may be accumulated an estimated 16,000 tons of sludge annually. Reported sludge volumes ranged from 20 to 5,000,000 lb per year on a wet basis. Only 5 respondents gave data which permitted calculation of weight on a dry basis. Going on the assumption that the average composition of the sludges from these 46 companies was 10 percent solids, it may be calculated that these 46 companies, in aggregate, produced 1,130 tons of dry sludge. If this average were preserved throughout the entire field of 20,000 metal finishing companies, annual production of sludge on a dry basis would range between 400,000 and 500,000 tons.

Significantly, twelve percent of the respondents have apparently worked out methods of selling their sludge or reclaiming metal values to achieve an economic advantage from the problem of sludge disposal. These companies, reporting that they practiced metal recovery, were further queried by letter to determine methods used. Response was poor with only one U.S. and one foreign company answering. The U.S. firm used ion exchange to recover precious metals from rinse waters and cementation on iron to recover copper from spent circuit board etching solution. The foreign firm indicated it segregated nickel and cadmium rinse waters. Nickel waste was precipitated, thickened, and filtered by vacuum. The company reported it produced about 440 lb of filter cake (presumably dry) containing about 40 percent Ni. This was sold to a refiner. Cadmium recovery at this foreign firm, now being installed, will consist of electrowinning cadmium from a dragout solution onto steel cathodes which will be recycled as anodes to the cadmium circuit. The company claims the economics for electrowinning and recycling cadmium in this manner are favorable and that cadmium pollution is significantly reduced. The foreign company has been unable to interest metal refiners in mixed sludges, however, claiming that refiners object to sludges containing zinc and iron.

The data given in Table 2 indicate the metals found in sludges and, to some extent, the frequency at which they may be expected to be encoun tered, i.e., chromium, copper, and nickel most frequently, zinc and cadmium less frequently, and the other metals more or less rarely.

Table 1. TABULATION OF QUESTIONNAIRE RETURNS

	Questions	Number of Companies	Percent of Total (150) Responses
(1)	Accumulate waste sludge	77	51
(2)	Controlled neutralization	37	25
(3)	Uncontrolled neutralization	35	23
(4)	Planning to install a treatment plant soon	50	33
(5)	Activity by local, state, or Federal agencies	103	69
(6)	Companies reporting annual sludge volume	46	31
(7)	Method of sludge disposal	88	58
	Public landfill or dump	32	21
	Private landfill or dump	45	30
	Sell for reclamation	8	5
	Pay to haul away	3	2
(8)	Reclaim metal values	11	7
(9)	(See Table 2)		
(10)	Cooperate with MFF	106	71

Table 2. REPORTED METAL CONTENTS OF SLUDES

Kind of Metal	Number of Companies	Percent of Total (150) Responses
Potentially Valuable Base Metals		
Copper	78	52
Nickel	80	53
Chromium	88	59
Zinc	58	39
Cadmium	63	42
Tin	36	24
Precious Metals		
Silver	16	11
Gold	10	7
Rhodium	1	1
Unspecified	2	1
Other		
Iron	8	5
Aluminum	10	7
Lead		4
Unspecified	2	1

The potentially valuable base metals of greatest interest to this study are listed in the first division of the table. The recovery of precious metals (second division of the table) from sludges constitutes a special problem and one that is probably being adequately handled by precious metal platers through collection and processing of sludges, either in-house or by custom refiners.

The recovery of iron and aluminum from metal finishing sludges is, of course, unthinkable. Lead recovery would be justified only under a very special set of conditions.

Of the potentially valuable metals it appears that the greatest potential for economic recovery is with copper, nickel, cadmium, and tin. Only under very special circumstances would chromium and zinc recovery be economically worthwhile.

Table 3 lists the data obtained in the questionnaire broken down by combinations of metals in the sludges.

These data indicate that most sludges produced up to now by metal-finishing companies are complex mixtures resulting from the combination of wastes from a number of plating lines. By percentage the distribution is as shown in the following tabulation:

Number of "Plating" Metals in Sludges Reported	Percent of Total Reporting	Cumulative
1	11.5	11.5
2	16.8	28.3
3	20.4	48.7
4	18.6	67.3
5	8.0	75.3
6	15.0	90.3
7	9.7	100.0

Of the metals cited, only nickel, copper, cadmium, tin, and the precious metals are of real economic significance, because of their price as well as the marketability and possible direct utilization of products from which they might be recovered. On a similar basis, zinc, chromium, and lead would have no economic attractiveness and very probably represent, in the majority of cases, economic liabilities in that they complicate chemical processing to recover the valuable metals. There

Table 3. ASSOCIATIONS OF PLATING METALS IN SLUDGE REPORTED

Single Metal		Four Metals	
Ni	3	Ni; Cu; Cr; Zn	5
Cr	7	Ni; Cu; Cr; Cd	5
Cd	1	Ni; Cu; Cr; Sn	2
Pm	2	Ni; Cu; Cr; Pm	2
	Total 13	Ni; Cu; Cd; Zn	1
Two Metals		Ni; Cr; Zn; Cd	2
Ni; Cr	4	Cu; Cr; Sn; Pm	1
Cu; Cr	3	Cu; Zn; Cd; Sn	1
Cu; Zn	1	Cr; Zn; Cd; Su	2
Cr; Cn	3		Total 21
Cf; Cd	2	Five Metals	
Zn; Cd	5	Ni; Cu; Cr; Zn; Cd	5
Cd; Pb	1	Ni; Cu; Cr; Zn; Pm	1
	Total 19	Ni; Cu; Zn; Cd; Sn	3
Three Metals			Total 9
Ni; Cu; Cr	14	Six Metals	
Ni; Cu; Cd	1	Ni; Cu; Cr; Zn; Cd; Sn	13
Ni; Cu; Pm	2	Ni; Cu; Cr; Zn; Cd; Pm	2
Ni; Cr; Cd	2	Ni; Cu; Cr; Zn; Cd; Pb	1
Cu; Cr; Cd	1	Ni; Cr; Zn; Cd; Sn; Pm	1
Cr; Zn; Cd	3		Total 17
	Total 23	Seven Metals	
		Ni; Cu; Cr; Zn; Cd; Sn; Pb	1
		Ni; Cu; Cr; Zn; Cd; Sn; Pm	10
			Total 11

may, however, be special cases which were not brought to light in this study--where chromium, lead, and zinc might be profitably won from sludges, as, for example, if they occurred singly in a segregated sludge and in such quantities to support adequate processing.

A review of Table 3 indicates that for most of the sludges reported, more or less complex processes involving chemical separations would be required.

SECTION VII

FIELD STUDIES

Field studies were made for three purposes:

(1) To augment the information gathered in the literature review, and in the survey by questionnaire, by personal conferences with company officials, inspection of waste treatment facilities, and the sampling and analysis of sludges produced.

(2) To obtain working samples of sludges for subsequent laboratory studies.

(3) To evaluate the weathering characteristics of a lagoon-stored sludge and to determine the extent of percolation of leachate from the sludge bed into underlying ground.

Treatment and Disposal Practices

This program included visits to plants, inspections of sludge lagoons, and the acquisition of actual sludges for use in the laboratory studies. Information relating to the wastewater treatment which results in sludge formation is summarized in Tables 4 and 5. Details of each plant are given in Appendix C (Plant Visitations and Sludge Characteristics).

As stated previously, one purpose of the field studies was to obtain a first-hand view of the problem, so as to augment the information gathered in the literature review and survey by questionnaire. Of the seven plants visited, six could be classified as multiple-operation metal-finishing plants employing electroplating (Tables 4, 5, 6, 7, 8, 9). One, an aluminum anodizing plant yielded little information helpful to this study, its sludge being largely aluminum hydroxide and diatomaceous earth used as filter-aid.

Characteristically, the lagoon-stored sludges from the metal-finishing plants doing plating or pickling (Plants A, B, C, E, and G) were found to be quite thin, containing only 2 to 4 percent solids. Laboratory filtration of some of these sludges produced filter cakes containing 10 to 16 percent solids. (Plant A, E, G). Several sludges (B and C) were oily and were not filtered but dried directly.

Table 4. TREATMENT AND DISPOSAL PRACTICES

Company	Cu	Ni	Cr	Zn	Cd	Sn	Pd	Other	Treatment of Wastewaters	Remarks
A	X	X	X			X	X	--	Cr^{+6} reduced to Cr^{+3} with bisulfite. Metals precipitated as hydroxides with CaO and/or NaOH, then to clarifier.	Mixed sludge to concrete and block-lined lagoon. Water 95 + %. Sludge periodically hauled to dump. Two lagoons used alternately.
B	X	X	X	X	X	X		Phosphating	Acid and alkaline wastewaters mixed. Sludge collected in sump. Unprecipitated metals plus unneutralized wastewater to sewer.	Sludge hauled to dump.
C	X	X	X		X			Ag plated Al etched Phosphating	Same as Company B.	Same as Company B.
D								Al anodizing	Sludge from caustic etch vacuum filtered.	Sludge hauled to dump.
E	X	X	X	X	X			--	Cr^{+6} reduced to Cr^{+3} with SO_2 or bisulfite. CN oxidized by Cl, first to CNO- finally to $Co_2 + N_2$. Metals precipitated as hydroxides, then to settling tanks.	Mixed sludge to earthen lagoon.
F	X(1)		X	X(1)				--	Cr^{+6} reduced to Cr^{+3}. Metals precipitated as hydroxides, then to settling tanks.	Four lagoons available. Two in service at a given time. Efficient dewatering. Sludge finally hauled to storage lagoon. Water 60%.
G			X	X	X			--	Cr^{+6} reduced to Cr^{+3} with bisulfite CN completely destroyed by Cl oxidation. Metals precipitated as hydroxides, then to settling tanks.	Two lagoons. When settling occurs in #1, then supernatant liquid runs into lagoon #2. Further settling here. Water finally discharged to stream. Water in sludge 95 + %.

(1) These metals are found in the sludge as a result of the pickling of brass and copper.

Table 5. SLUDGE CHARACTERISTICS

Company	Stored Sludge % Solids	Stored Sludge Other	Filtered Sludge[2] % Solids	Dried Sludge Composition[4] Cu	Ni	Cr	Pd	Sn	Ag	Zn	Cd	Fe	Al
A	2 to 4	--	10-13	3-5	3-5	5-15	0.1[5]	0.7	--	--	--	--	--
B	4	Organic Material Grease and Oil?	-- --	0.3	0.3	0.7	--	3	--	3-5	0.2	3-6	--
C	4	Organic Material Grease Oil	-- --	3-5	1	1	--	--	0.2	--	0.5	3-6	--
D	OK[3]	Filter Aid	32[3]	--	--	--	--	--	--	--	--	--	5-15
E	3	Yellow-Green	11-13	1	2-4	5-15	--	0.04	--	5-10	0.3	--	--
F	Ca 40[1]		--	2-6	0.1-0.2	5-15	--	0.1-0.3	--	0.5-1.0	--	--	--
G	3-4	Segregated Variable Color	16	0.1-0.2	--	5-15	--	0.1	--	3-5	3-5	--	--	--

(1) Dried in lagoon, presumably by seepage and/or evaporation.
(2) Samples taken from lagoon filtered through Whitman #2 paper on Buchner funnel by vacuum for three minutes after visible filtrate had stopped.
(3) Filtered through commercial rotary vacuum filter, using diatomaceous earth, at the company's plant.
(4) Semi-quantitative spectrographic analyses. Values shown in columns are for those metals used in plant.

Table 6. SEMI-QUANTITATIVE SPECTROSCOPIC ANALYSIS OF DRIED SLUDGE

Company	Weight Percent											
	Cu	Ni	Cr	Sn	Pd	Zn	Cd	Ag	Al	Mn	Fe	Ba
A	3-5*[a]	3-5*	5-15*	0.7*	0.1*	<0.1	<0.1	<0.005	0.03	0.01	0.2	0.02
B	0.3*	0.3*	0.7*	3.*	<0.1	3-5*	0.2*	<0.005	2.	0.05	3-6*	0.4
C	3-5*	1.*	1.*	0.05	<0.1	0.1	0.5*	0.2*	3-5*	0.1	3-6*	0.04
D	0.03	0.01	0.1	<0.01	<0.1	<0.1	<0.1	<0.005	5-15*	0.02	1	0.01

	Weight Percent										
	B	Si	Mg	Pb	Bi	Mo	Ca	Na	Ti	Zr	Co
A	0.05	0.5	2.	0.02	<0.01	<0.01	5-10	0.5	<0.01	<0.01	0.01
B	<0.01	2.	0.3	0.2	<0.01	<0.01	5-10	0.5	0.1	<0.01	<0.01
C	<0.01	3.	0.3	1	0.05	0.02	10-20	0.1	0.2	0.01	0.01
D	<0.01	5-15	1	<0.01	<0.01	<0.01	2	1	0.1	<0.01	<0.01

(a) Elements whose values appear with an asterisk (*) beside them are those elements which one would expect to be present on the basis of the metal finishing operations at a given plant.

Table 7. SEMI-QUANTITATIVE SPECTROSCOPIC ANALYSIS OF DRIED SLUDGE

Sample	Weight Percent											
	Ca	Ni	Cr	Zn	Cd	Sn	Fe	Mn	Pd	Ag	Al	Ba
E-1 (near inlet)	1.*[a]	2.-4*	5.-15.*	3.-5.*	0.2*	0.04	2.-4.	0.03	<0.1	<0.005	0.2	0.01
E-2	1.*	2.-4.*	5.-15.*	5.-10.*	0.3*	0.04	2.-4.	0.05	<0.1	<0.005	0.3	0.01

	Weight Percent											
	B	Si	Mg	Pb	Bi	Mo	Ca	Na	Ti	Zr	Co	Sr
E-1 (near inlet)	0.03	2.	1.	0.04	<0.01	<0.01	3.-6.	0.5	<0.01	<0.01	<0.01	0.04
E-2	0.02	2.	1.	0.03	<0.01	<0.01	3.-6.	0.5	<0.01	<0.01	<0.01	0.02

(a) Elements whose values appear with an asterisk(*) beside them are those elements which one would expect to be present from the metal finishing operations.

Table 8. SEMI-QUANTITATIVE SPECTROGRAPHIC ANALYSES OF THREE SAMPLES OF DRIED SLUDGE

Sample Number	Location and Depth[a]	Weight Percent											
		Cu	Ni	Cr	Cd	Zn	Sn	Pd	Ag	Al	Mn	Fe	Ba
F-1	II Center 1-6 inches	4.-6.*[b]	0.2*	5.-15.*	<0.1	1.*	0.3*	<0.1	0.005	2.	0.02	0.5	<0.01
F-2	II Center 12-18 inches	4.-6.*	0.1*	5.-15.*	<0.1	0.5*	0.3*	<0.1	<0.005	4.	0.01	1.	0.03
F-3	II N.W. Corner	2.-4.*	0.2*	5.-15*	<0.1	0.5	0.1	<0.1	<0.005	2.	0.02	1.	0.01

		Weight Percent											
		B	Si	Mg	Pb	Bi	Mo	Ca	Na	Ti	Zr	Co	Be
F-1	Center 1-6 inches	0.02	2.-4.	0.5	0.04	<0.01	<0.01	5.-10.	0.1	0.2	<0.01	<0.01	0.02
F-2	Center 12-18 inches	0.01	5.-15.	0.5	0.04	<0.01	<0.01	5.-10.	0.3	0.5	<0.01	<0.01	0.02
F-3	N.W. Corner 12 inches	0.02	2.-4.	0.7	0.03	<0.01	<0.01	5.-10.	0.3	0.2	0.01	<0.01	0.01

(a) This refers to the location in the storage lagoon from which the sample was taken and to the depth from which the sample was taken.

(b) Values that appear with an asterisk beside them (*) are those elements which would be expected on the basis of the metal finishing operations in use.

Table 9. SEMI-QUANTITATIVE SPECTROSCOPIC ANALYSIS OF DRIED SLUDGE SAMPLES FROM COMPANY G

	Cu	Ni	Cr	Cd	Zn	Sn	Pd	Ag	Al	Mn	Fe	Ba	B	Si	Mg	Pb
G-1 Southeast	0.1	0.03	5.-15.	3.-5.	3.-5.	0.1	<0.1	<0.005	0.07	0.03	2.	<0.1	<0.01	2.-4.	0.2	0.04
G-3 South Center	0.2	0.05	5.-15.	3.-5	3.-5.	0.1	<0.1	<0.005	0.07	0.04	4.	<0.1	0.01	2.-4.	0.3	0.05

	Bi	Mo	Ca	Na	Ti	Zr	Co	Be
G-1 Southeast	<0.01	<0.01	5.-.10	0.1	0.2	0.01	<0.01	<0.01
G-3 South Center	<0.01	<0.01	10.-20.	0.1	0.1	<0.01	<0.01	<0.01

Copper composition of the metal-finishing sludges, on a dry basis, from plants in which copper was either plated or leached to pickle (A, B, C, and F), ranged from 0.3 percent to 6 percent as determined by semi-quantitative spectrographic analyses, with most of the values ranging between 2 and 5 percent. The low value shown for copper in the sludge from plant B (0.3 percent) may reflect a relatively minor copper circuit within the plant or the loss of copper to the sewer.

Variations in the nickel analyses between 0.3 and 5 percent of those plants plating nickel (Plant A, B, C, and E) is probably due to similar causes. The same applies for those plants plating chromium. The quantity of palladium apparently present in the dried sludge from Plant A, which plated a thin tin-palladium layer on plastic in one of its unit operations, is surprisingly high and may be the result of analytical error. If indeed the sludge has 0.1 percent of palladium in it, or 2 lb. per ton, avoirdupois, this is the equivalent of about 30 troy oz per ton of palladium. The technology and economics of recovering palladium, if it does exist in significant quantity in such sludges would require a specific study. The concentration of tin in the sludge from Plant B, about 60 lb per ton, could also be attractive economically. The silver in the sludge from Plant C amounting to about 60 troy oz per ton is also worth further consideration. The recovery of palladium, tin, and silver, if they did exist in significant concentrations in sludges, would best be studied specifically.

There is considerable doubt the quantities of Zn and Cr in the various sludges examined could be profitably exploited. Aluminum and iron are, of course, valueless in such sludges.

Sludge Weathering and Leaching

A major objective of this work was to make on-site studies which would determine the extent to which sludge in a given storage lagoon would yield its toxic metal values to solution in rain, runoff, or intruding ground water and so contaminate aquifiers.

The literature search had uncovered a report of the U.S. Geological Survey that discussed an example of ground water contamination by plating wastes held in storage basins or lagoons in Nassau County, New York.

The uppermost aquifer (water bearing bed or stratum) in the South Farmindale-Massapequa area consists chiefly of permeable deposits of sand and gravel having a contaminated region ranging from 60 to 140 feet thick. The water table was about 1 to 2 feet below the bottom of the lagoons in December, 1962, a seasonably low period, but in spring the water table may rise above the bottoms of the lagoons. Plating

wastes were found to have seeped down from the lagoons into the aquifer intermittently since 1941. This seepage resulted in a plume of contaminated water some 4,300 feet long, up to 1000 feet wide, and as much as 70 feet deep, extending downgrade to the headwaters of Massapequa Creek. The concentration of polluting metals in this plume were often as high as 40 mg/l.

Originally this plating wastewater was untreated. Maximum treatment began in 1958 apparently resulting in the formation of sludge which effectively sealed the lagoon sides and bottom. Since the start of chromium treatment, concentrations reportedly decreased to less than 5 mg/l in most of the plume.

Work to determine whether such weathering and leaching had occurred was done at the Company F lagoons. This site seemed particularly worth investigating because the company had been utilizing these lagoons for over 10 years.

In carrying out this investigation, shale structures underlying Company F sludge lagoons were core-drilled to approximately 20 feet below the bottom of the lagoon. The cores were analyzed for heavy metal components known to be present in the stored sludge.

Details of the core-drilling procedure and analytical data are shown in Appendix C, "Field Studies - Sludge Weathering and Leaching Studies".

No evidence of the leaching of metal ions into ground water was found in this instance.

This is believed due to the fact that the sludge was, in the first place, adequately treated by reduction and neutralization when stored, and secondly, that the stratum underlying the lagoons was relatively impermeable.

SECTION VIII

LABORATORY STUDIES

Work in the laboratory comprised a study of the leachability of sludge samples obtained from the plants in the field studies; and detailed investigations of three routes to the recovery of metals suggested by the literature study to have some promise. These were electrowinning, cementation, and liquid ion exchange.

Leaching

The leaching experiments were made on dried samples of sludge from each of the seven plants that had been sampled. Tables 6 through 9 show the complete semi-quantitative spectroscopic analysis of these sludges was not made.

These dried sludges were leached under a variety of conditions in mineral acids, solutions of ammonium salts, ammonium carbonate, and sodium hydroxide. Sodium hydroxide was used in only a few runs for the purpose of removing zinc.

The results, in general, indicated that copper, nickel, and chromium in all the sludges were readily and almost completely dissolved in mineral acids and ammonium carbonate solutions, as might be expected. Residue weights after leaching varied from sludge to sludge and were dependent on the type of leaching medium used.

The results of the leaching tests on the dried sludges are summarized in Table 10 and are presented in more detail in Appendix D, "Selected Leaching Experiments".

A few leaching tests were made on fully incinerated sludges, using mineral acids and ammonium carbonate solutions. Details of these are also included in Appendix D, "Selected Leaching Tests".

The results of these leaching experiments indicated that sulfuric acid would yield acceptable extraction of copper, nickel, and chromium when applied to undried or dried sludge. There is the possibility, however, that was not explored, that calcined sludge might not respond as well owing to the possible formation of silicates or ferrites during the calcination Although fairly drastic conditions with respect to time, acid concentration, and temperature were used in most of the sulfuric acid leaching tests, it is believed that in practice, the precipitated

Table 10. SELECTED LEACHING EXPERIMENTS ON DRIED SLUDGES

Run No.	Sludge Designation	Wt. gms.	Leaching Conditions				Leaching Results
			Media	Vol. ml.	Temp., F	Time, hrs.	% Weight Lost
1	A	25.0	1:1 H_2SO_4	100	170	16	67.6
2	"	25.0	"	150	"	11	60.4
3	"	25.0	"	150	"	11	67.0
5	"	100.0	20% H_2SO_4	1000	145	17	69.8
7	"	10.0	20% $(NH_4)_2CO_3$	200	175	6	21.6
8	"	10.0	20% $(NH_4)CL$	200	"	6	25.4
9	"	10.0	20% $(NH_4)_2SO_4$	200	"	6	2.8
10	"	10.0	20% $(NH_4)_2CO_3$	200	70	168	22.3
11	"	10.0	"	200	70	24	22.3
12	"	10.0	7% $(NH_4)_2CO_3$ 14% NH_4OH	200	200	23	23.3
13	"	10.0	35% $(NH_4)_2CO_3$	200	70	71	34.3
17	B	15.0	20% $(NH_4)_2CO_3$	200	150	6	17.5[a]
19	C	15.0	"	200	150	6	7.9[a]
23	E-1	10.0	1:1 H_2SO_4	100	70-150	8	50.3
24	E-2	10.0	1:1 H_2SO_4	100	70-150	8	30.2
25	E-1	10.0	35% $(NH_4)_2CO_3$	200	70	69	21.3
26	E-2	10.0	"	200	70	69	25.8
27	E-2	10.0	25% NaOH	100	150	2	32.0[b]
28	Residue from 27	----	1:1 H_2SO_4	100	150	2	85.0
29a	E-2	25.0	25% NaOH	250	150	1	----
			1:1 H_2SO_4	40	140	1	86.4[b]
30	F-1	10.0	1:1 H_2SO_4	150	150	1.5	51.6
31	F-2	10.0	"	150	150	1.5	47.1
32	F-2	10.0	23% $(NH_4)_2CO_3$	125	150	4	20.1
33	G-1	10.0	1:1 H_2SO_4	150	150	1.5	61.0
34	G-3	10.0	"	150	150	1.5	40.0[c]
35	G-1	10.0	20% H_2SO_4	100	75	24	1.0
36	G-1	10.0	20% H_2SO_4	100	175	24	40.0
37	G-1	10.0	23% $(NH_4)_2CO_3$	125	75	2	6.3

Note:

(a) These sludges contained oil and grease. On leaching with acid they evolved H_2S.

(b) NaOH leach used to predissolve zinc.

(c) Evolved H_2S on leaching with acid.

hydroxides present in typical metal-finishing plant wastes will be quickly and readily solubilized under much milder conditions.

In the leaching runs made with ammonium carbonate solution, copper and nickel extraction were generally good while trivalent chromium remained with the residue. This selectivity for copper and nickel over chromium may be an advantage of the ammonium carbonate system. As in the sulfuric acid leaching experiments, drastic conditions were used in the ammonium carbonate leaching experiments. It is believed that temperatures not much above ambient and relatively short leaching periods should suffice to extract the bulk of nickel and copper present as hydroxide in a conventional metal-finishing sludge. A disadvantage of the ammonium carbonate system is that it will readily dissolve zinc hydroxide from such sludges. Experience has shown that zinc is likely to be more of an economic liability than an asset in the recovery of metals from mixed wastes. Another possible disadvantage, one that was not explored, is that ammonium carbonate can react with calcium sulfate to form ammonium sulfate and calcium carbonate, with the result that ammonium sulfate might be expected to build up in the leach liquor. The leaching experiments also served to evaluate the various sludges from the different plants for applicability to the recovery work.

Sludges from Plants B and C which were mixtures of miscellaneous plant wastes containing oil, grease, and sulfuric materials, and which were not the result of controlled treatment, were considered too atypical for further work. The sludge from Plant D, largely an aluminum hydroxide-dialomaceous earth mixture originating from the treatment of waste caustic used to etch aluminum was also discarded from consideration.

Although it was noted that some of the sludges contained possibly economic quantities of Sn, Pd, and Ag, no effort was made in these leaching studies (or in subsequent recovery studies) to study their behavior. The recovery of such metals properly requires a pointed investigation.

The sludge from plants A, E, and G were selected for starting materials in the recovery experiments.

SECTION IX

RECOVERY EXPERIMENTS

Three approaches to the recovery of copper and nickel were investigated. These were electrowinning, cementation, and liquid ion exchange. The recovery of chromium was not considered.

Electrowinning

For reclamation of metal values from metal-finishing (large electroplating) wastes, electrowinning appears to be a readily feasible approach. Electroplating plants have DC electrical power available; the process of electrowinning is a process closely allied to electroplating; if the leach liquor requires minimal preparation, electrowinning can be less costly and more direct than many other methods of separation.

Preliminary Experiments

Copper, being fairly noble, can be electrodeposited from a variety of solutions. The first solution from which it was successfully separated in the work was the acidic solution which resulted from 1:1 sulfuric acid leaching of sludge A. After filtering off the calcium sulfate, the copper-containing filtrate was used without any modification and electrowinning took place at constant current and room temperature. The deposite on a rotating stainless steel cathode was powdery. Agitation of the solution and raising the temperature from 75 F to 122 F resulted in an improved copper deposit. At a current density of 2 amps/sq ft, an efficiency of 85 percent was achieved. Very high current densities are not required but a ten-fold increase in this initial current density was used in later experiments. Additional experiments on the electrowinning of copper from sulfuric acid leach solution resulted in a better deposit by use of small gelatin additions. A current density of 18 amps/sq ft and a temperature of 126 F were used in these experiments. It was not deemed necessary to produce a deposit comparable to a good grade electroplate. If a powdery deposit forms, it can be removed from the rotating cathode by a "doctor" blade which in effect scrapes the powder from the cathode. With a horizontal rotating cathode which is only partly immersed in the solution the copper could be collected in a trough which runs along the side of the blade away from the cathode. Where the deposit is adherent and fairly smooth, a thin copper starting sheet can be bent around the rotating cathode. After a certain thickness

of copper has been deposited, the starting sheet with the extra copper can be removed and sold as copper scrap.

With all the copper removed from the leach liquor by electrowinning, the next step was to attempt to electrowin nickel. Nickel could not be electro-deposited from the sulfuric acid solution under any of the conditions applied in the preliminary work. The failure was attributed to the presence of interfering elements, possibly chromium.

It was found, however, that both copper and nickel could be deposited from ammonium carbonate leach solution with minimal modification of the solution. With constant current electrolysis, the cathode potential changed slowly with time to more negative values as the solution became depleted in copper. The result of this was that although copper alone deposited at first, gradually the material depositing contained more and more nickel, and finally consisted of nickel alone. Such a constantly varying deposit of copper and nickel could probably be disposed of by sale to makers of cupro-nickel.

In view of these promising preliminary results, the electrowinning work was focussed on electrolysis from ammonium carbonate solution.

Electrolysis of $(NH_4)_2CO_3$ Leach Solutions

Three-Compartment Cell Runs

Following preliminary experiments with $(NH_4)_2CO_3$ leach liquors, a three-compartment electrolysis cell was constructed from Lucite (Figure 1). The general method for operating this cell is to place the $(NH_4)_2CO_3$ leach liquor, including the insoluble portion, in the center compartment. The slurry is agitated by the magnetic stirring bar, and the solution containing copper and nickel passes through the diaphragms to the anode and cathode compartments. For the first experiments, Number 2 Whatman filter paper served as diaphragms. The advantage of the three-compartment cell was that filtering and electrowinning took place simultaneously.

The first experiments in which the three-compartment cell was used were run at constant current. As noted previously, copper and nickel codeposited from ammonium carbonate solution, the composition of the deposit depending on the elapsed time. The rate of diffusion through the filter paper membrane initially selected was too slow to keep the copper concentration constant in the cathode compartment. At the selected current

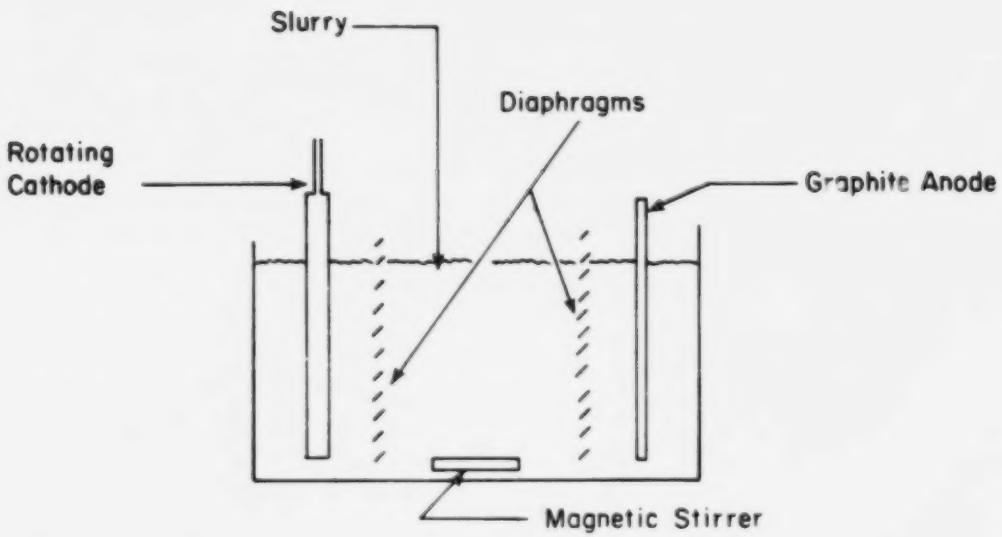

Figure 1. Schematic drawing of
3-compartment cell

density, the deposition rate exceeded the rate of diffusion of copper into the cell compartment. At 20 amps/sq ft, the efficiency of 43 percent for the copper-rich stage of electrowinning was judged to be too low. The efficiency of the nickel-rich deposition averaged somewhat higher, being 56 percent.

The low current efficiency was fairly constant throughout the period of electrodeposition. This was found to be related to the rate at which the surface of the rotating cathode moved through the solution. In the experiments just cited, cathode rotation was at a rate of 130 linear inches per minute. This expression of movement is used rather than rpm because several diameters of cathode were used.

Runs in Three-Compartment Cell

The three-compartment cell was then modified, so that after electrowinning had been conducted for 1 hour, the catholyte could be pumped continuously to the center compartment. This amounted to recycling of the partially stripped ammonium carbonate solution from the cathode compartment to the center compartment so that additional sludge (now maintained as a slurry in the center compartment) could be dissolved, and thus flow through the diaphragm as enriched leach liquor to the catholyte. Fresh sludge was added to the center compartment periodically. Typical drop in efficiency with time for this type of cell is shown in Figure 2.

Nylon diaphragms were substituted for the paper diaphragms in the three-compartment cell. The rate of diffusion was more rapid through the nylon, but some of the fine particles of sludge were not retained, resulting in a dilute of light slurry in the cathode compartment. At 21 amps/sq ft and 115 F, with a rotating cathode linear speed of 259 linear inches/minute, the cathode efficiency started off at 32 percent and became lower with time. By increasing the cathode linear speed periodically the efficiency was restored to something near the original value.

Electrolysis from a Slurry in a Single Compartment Cell

The foregoing experience suggested that it might be of value to study the electrowinning of copper and nickel from a relatively heavy slurry in a single compartment cell. The slurry was agitated by a magnetic stirrer so the degree of agitation was greater than indicated by the cathode surface speed. Results were favorable in that nickel and

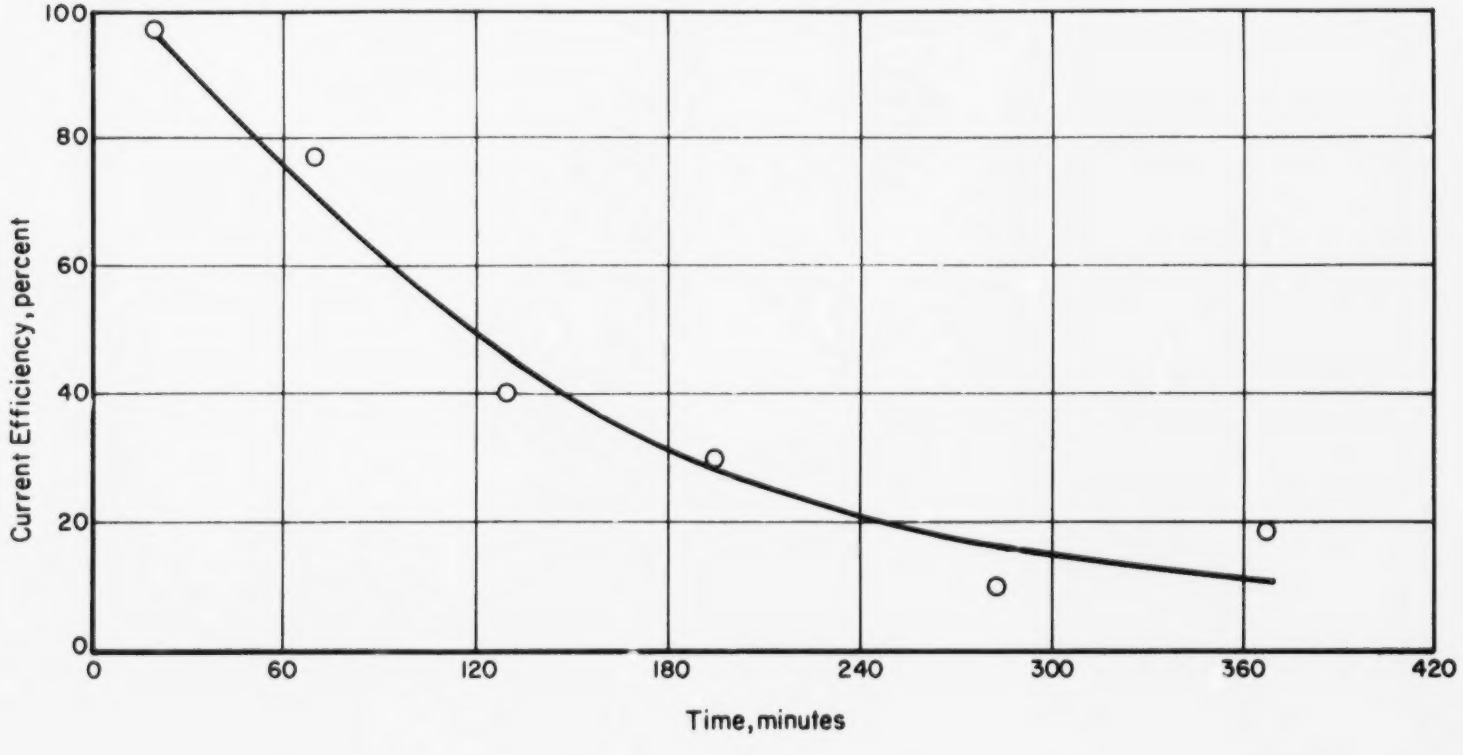

Figure 2. Current efficiency as a function of time

copper were effectively deposited without serious contamination from suspended solids. This approach, however, requires additional work.

Electrolysis of Nickel and Copper by Cathode Potential Control

Copper and nickel can be separated by means of controlled cathode potential electrowinning. This requires an electronic instrument called a potentiostat which will maintain a constant potential between the cathode and some reference electrode such as the saturated calomel electrode (SCE). By holding the cathode potential at about 0.3v relative to the SCE, copper alone will deposit. When all the copper has been removed from the solution, then the potentiostat is adjusted to give the cathode a more negative potential and nickel will deposit. A schematic drawing of the apparatus used is shown in Figure 3.

Controlled cathode potential electrowinning was used in one run with the ammonium carbonate slurry of sludge A. The maximum cathode surface speed (325 inches/minute) was used throughout the experiments. The cathode potential was held constant at -0.75 volt versus SCE for the electrowinning of copper. This is higher than the -0.3 volt given above as the standard value, but the higher voltage was used to achieve a higher current density. The solution consisted of 1 liter of slurry containing 300 g/l of $(NH_4)_2CO_3$ and 50 g of sludge A. The slurry was stirred for 1 to 2 hours prior to start of electrowinning. The initial current density was 30 amps/sq ft and the average current density for the 7.41 hours run was 11.5 amps/sq ft. Temperature was constant 111 F, and gelatin solution was added periodically to maintain the concentration at 1.0 g/l. Again, a magnetic stirrer was used to keep the sludge in suspension. Periodic additions of sludge were made to replace the copper that was deposited on the rotating cathode. Taking the copper content of the dried sludge to be 5 percent, the recovery of copper was calculated at a value slightly over 100 percent.

The cathode potential was then raised to -1.25 volts versus SCE and the electrowinning was continued. The initial current density was 25 amps/sq ft and the average for the 5.91 hour run was 13.8 amps/sq ft. Taking the nickel content of the dried sludge to be 5 percent, 93 percent of the nickel theoretically available was recovered. Probably a small amount of nickel codeposited with the copper toward the end of the first run, thus accounting for the recovery of over 100 percent. The total weight of metal recovered by electrowinning was calculated as 100.5 percent of the copper and nickel present. Codeposition of nickel with copper could be prevented by using a lower cathode potential, possibly 0.5 volt.

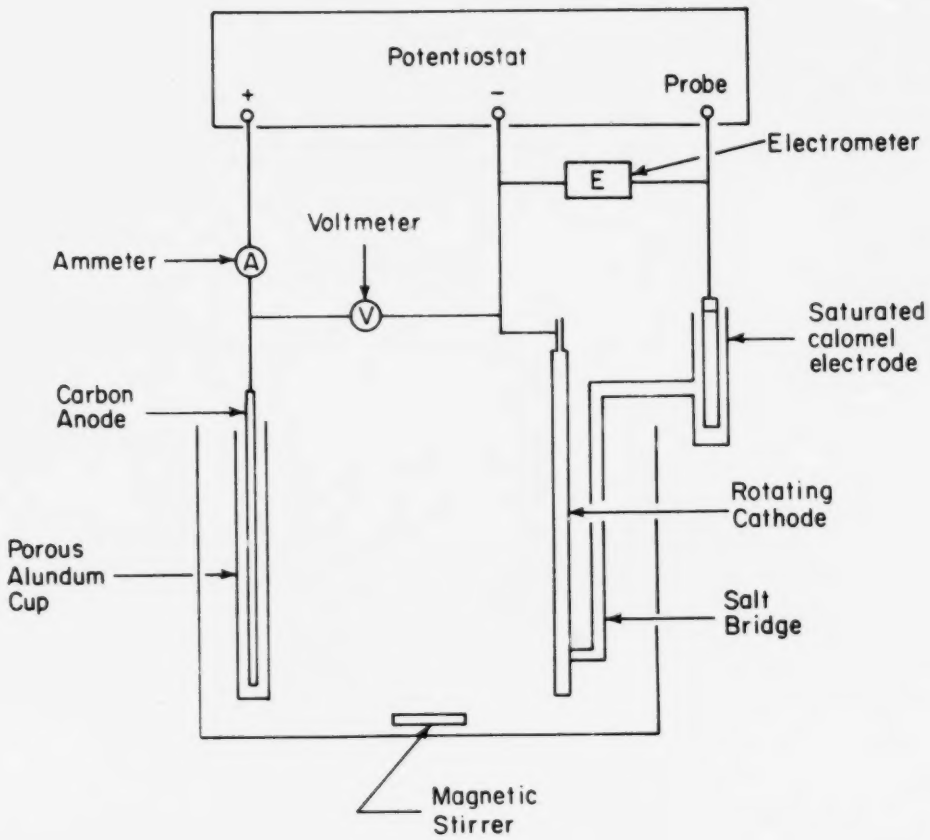

Figure 3. Schematic drawing for apparatus used for constant cathode potential electrowinning

In both cases, the deposits were acceptable for the purpose of resale. Some copper flaked off the stainless steel cathode but this is easily recovered by filtration.

A few exploratory electrowinning experiments were also made on stripping liquors produced in a parallel liquid ion exchange study but these were marked by extremely low efficiency due, it is believed, to residual organics (naphthenic acid) carried into the stripping solution. Further work on this phase of the study was deferred.

General conclusions from the electrowinning studies were that while the approach held promise, considerable amounts of additional development work would have to be done to establish the lines of a process that would be technically and economically acceptable.

Cementation

In extractive metallurgy, copper is often separated by adding metallic iron to the copper-containing acidic solution. Copper being more noble precipitates in the metallic state and iron goes into solution according to the following equation

$$Cu^{++} + Fe^{o} \longrightarrow Cu^{o} + Fe^{++}$$

In the single experiment performed to investigate the concentration of copper, 100 g of dried sludge A were dissolved in 1 liter of 20 percent H_2SO_4 solution. Calcium sulfate was removed by filtering the mixture. The iron was shredded pieces of 5 mil-thick low carbon steel. The solution was heated to 130 F and was stirred slowly. The excess undissolved iron was removed by magnetic means and the solution filtered to recover the copper. The recovered copper weighed 4.15 grams. It was in the form of a "mud" and could be washed so that it was fairly pure.

The use of cementation to separate copper can be questioned because one metal in solution is being replaced by another and this can be viewed as not lessening the potential for pollution. However, iron is much less toxic than copper. In addition, many sludges already have iron present to the extent of several percent. The big advantage of cementation is its relatively low cost. In specific instances, however, cementation would be applicable. A limited amount of work was also done to investigate the cementation of cadmium. Dried sludge G contains 3 to 5 percent cadmium. The sludge was dissolved in 20 percent sulfuric acid solution. After filtering off the $CaSO_4$ the filtrate was electrolyzed at a controlled cathode potential of -0.3 volt to separate the small

amount of copper. Following this the cadmium was cemented by the addition of powdered zinc. The cadmium metal was then filtered off. Recovery appeared to be good, the reclaimed cadmium being 4.04 percent of the original quantity of dried sludge. In the case of cadmium cementation, cadmium is replaced in solution by zinc. However, zinc is already present in the solution and at a scrap price of about five cents a pound it is hardly worth a special effort at recovery.

Liquid Ion Exchange

The possibility of employing liquid ion exchange for the recovery of potentially valuable metals in metal-finishing wastes was investigated in some detail in the laboratory. Both sulfuric acid and ammonium carbonate leach liquors were employed as feed stock.

The laboratory work, described in detail in Appendix D, "Liquid Ion Exchange", brought to light a host of problems including formation of precipitates, emulsions, the necessity for precise pH admustment to obtain selectivity, the carryover of extraction into stripping solutions, in some cases the necessity for large numbers of extraction and stripping stages, incomplete separations, etc.

On the basis of what has been revealed by the laboratory studies, it is highly doubtful that liquid ion exchange could be considered a generalized process for treating metal-finishing sludges.

SECTION X

ECONOMIC STUDIES

Preliminary economic studies were made to determine the cost of small-scale processing sludges of the compositional range encountered in the sludges obtained from the various companies. Details are presented in Appendix E.

The results of this study indicated that a batch experimental operation treating 100 lb per day of dry solids (equivalent to 3,330 lb/day of wet sludge would cost about $85 per day including amortization. Plant cost for this small unit was estimated at about $15,000.

Metal recovery per day was assumed to be 5 lb of copper and 0.3 lb of nickel. Obviously at this scale, type of operation, and with a sludge of the composition assumed, there are no economics to consider.

If the scale of operation were increased ten-fold to about 1,000 lb per day of dry solids, of material containing 5 percent copper and 3 percent nickel instead of 0.3 percent, and some credit be taken for chromium, economics might be extrapolated as follows:

Capital Cost of Plant	$90,000.00	
Operating costs exclusive of labor	177.00	
Labor (3 times that for 100 lb/day plant)	180.00	
Total daily operating cost		$ 357.00
Revenue from Cu at 50 cent/lb (50 lb)	$ 25.00	
Revenue from Ni at $1.00/lb (30 lb)	30.00	
Revenue from Cr at 10 cent/lb (100 lb)	10.00	
Total revenue		$ 65.00

Further extrapolation to 10,000 lb/day of dry solids yields:

Capital cost of plant	$540,000
Operating costs exclusive of labor	1,200

Labor (3 times that for 1,000 lb plant)	$ 540	
Total daily operating cost		$1,740.00
Revenue from copper, nickel, chromium		650.00

The inescapable conclusion is that a process of the type studies operating on the sludges considered would not even approach good economics.

SECTION XI

APPENDICES

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APPENDIX A

LITERATURE REVIEW

The literature search began with a perusal of the large number of punched cards which had accrued as a result of a previous search on metal-finishing waste treatment[1]*. This previous search, although primarily seeking knowledge of methods for treating metal-finishing liquid wastes (rinses, etc.) was nevertheless quite comprehensive, and some pertinent information was obtained.

The search continued throughout the course of the project as new technical requirements appeared.

A complete set of "Selected Water Resources Abstracts"[2] which began publication in 1968 was available, and these have been studied through to the current issue. "Pollution Abstracts"[3] which began publication in 1970 also has been consulted. "Chemical Abstracts" was used in searching for specific topics and was not used for a comprehensive search because such a search had been made in preparing reference (1). The British "Water Pollution Abstracts"[4] was checked from 1947 (Volume 19) through May, 1971 (Volume 44). Also of value were the yearly bibliographies or reviews of literature relating to plating wastes as given in "Plating"[5] and the "Journal of the Water Pollution Control Federation"[6].

For specific topics, such as, for example, the chemistry of a given element or the solubility of a compound, a series of general references was consulted.[7-17] For specific operations, such as electrodeposition, filtration, etc., a number of references were available.[7, 18-24]

Very little was found on the subject of reclamation of metal values from metal-finishing waste treatment sludges. These sludges, resulting from the precipitation of soluble metals as hydrated oxides, are usually hauled away to a public or private landfill. In some locales, where stringent pollution laws are not in effect, much of the sludge finds its way into the sewer system or is run directly into a nearby stream.

Pepperl[25] describes the incineration of electroplating sludges containing copper, nickel, zinc, chromium, iron, and cyanides. It was

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* Numerical figures in parentheses relate to references in the bibliography (Appendix F).

first necessary to filter the sludge to reduce the water content to 55 to 60 percent. This was done in a filter press or vacuum filter. The incineration took place in a specially designed fusion cone incinerator which used combustibles such as saw dust, wood shavings, varnished papers, oil sludges, and varnish sludges, all of which were waste products in the factory producing the electroplating sludges. Suitable precautions were taken to minimize air pollution from the incineration. The sludges containing about 60% water were incinerated at 900 to 1100 C. The volume of the materials was substantially reduced, the final volume being about the seventh of the initial volume. The material thus required less land for disposal and was decontaminated, that is, the cyanides were completely destroyed and the metal compounds were converted to oxides which, because of their low solubility, pose less threat to the ground water. The author did mention in passing that metal reclamation was a possibility. He did not, however, give any indication of this having been done. The sludges were comparable in composition to the sludges used in the experimental work on this project.

Rehm and Nietz[26] described the low-temperature incineration of sludges. This work was done at temperatures of 200 C or below. They found that, if the sludge is heated above 200 C, some of the trivalent chromium is oxidized to hexavalent chromium in the presence of alkali. The sludge was slightly alkaline since it had been treated with NaOH or CaO to precipitate the hydroxides. When incinerated sludge, containing highly soluble chromates, is dumped in a landfill the chromium can find its way into the ground water. However, the low-temperature incineration (if it can really be termed this) resulted in a large reduction in volume, the final volume being reported as 1/13 of the initial volume. Thus, a piece of land which would accommodate a 10-year accumulation of sludge could not contain a 130-year accumulation.

Weiner[27] also pointed to a reduction in volume and cautioned about the danger of solubilizing zinc and chromium by heating sludge above a certain temperature.

Niemetz[28] in a long discussion about sludge handling discussed dewatering and incineration briefly. He mentioned the high cost of dewatering, but gave no definite figures.

J. J. McGrath[29] dealt with treatment of sludges at a brass mill. These resulted from pickling of brass, and the sludge contained iron, copper, chromium (from the chromate solution used in surface treatment of brass), zinc, and calcium. This sludge was partially dewatered by a rotary vacuum filter to a cake containing about 40 percent solids. Some 28 tons of filter cake were produced per month. Although the

author did not mention it, it was supposed that the sludge was dumped at some landfill or other appropriate site. The author proposes developing a use or market for the filtered sludge.

At this point it is appropriate to look to those references which discuss the reclamation of metal values from metal-finishing wastes before they are converted to sludge. The reference just cited (29) was one of these. McGrath recovered copper by cementation on iron. Iron in the divalent state also serves to reduce hexavalent chromium. About 5 tons net weight of copper were recovered per month.

Several papers which describe reclamation of metal from waste solutions were found. In a paper published in 1917[30] Jones described the electrolytic recovery of copper (and sulfuric acid) from copper mill pickling solutions. In one run of 60 days (10 hours per day) for an expenditure of 1600 kilowatt days of electricity 3,755 pounds of copper were recovered. This is equivalent to slightly less than 1 pound per kilowatt hour. The efficiency was 72 percent from a solution containing 14 percent sulfuric acid and 3.5 percent copper. The electrowinning was done on a continuous basis at 6.2 amps/sq ft and 2 volts. Other examples of recovering copper from pickling solutions are given in a publication of the British Non-Ferrous Metals Research Association[31]; and those which have been consulted are listed here (32, 33, 34, 35, 36). All of these discuss the electrowinning of copper from waste solutions, and relevant information in these publications was used in choosing initial experimental conditions for this program.

Sierp[32] preferred a copper concentration of 2 percent with the sulfuric acid at 5 percent. A good copper deposit was obtained at 5 amps/sq ft and 2.3 volts in the presence of up to 10 percent zinc. Recovery of copper took place at almost 100 percent of theoretical efficiency. The solution was agitated by pumping. The anodes were 8 percent antimonial lead. Sierp calculated that the energy requirement was about 1.9 kwh per pound of copper deposited but he includes conversion losses (a-c to d-c), distribution losses, etc.

Other references [33, 34, 35, 36] give data which are in approximate agreement with the findings cited in the above two papers.

Muller[37] also discussed waste recovery in the copper and brass industries. He described a transportable electrolytic copper reclamation unit for use in large plants where pickling units are scattered. He found recovery of zinc by electrowinning from acid baths was somewhat difficult and since the scrap value of zinc is low, he concluded that the effort might not be economically feasible.

Wise[38] and Wise and Dodge[39] studied the reclamation of metal values in the brass and copper industry. The first of these two papers describes how reclaimed electrolytically, copper was deposited on brass chips by cementation (in this process copper is displaced from solution by the zinc in the brass), and trivalent chromium was oxidized to the hexavalent form by roasting[38]. The zinc was electrodeposited from acid sulfate solutions and no great difficulty was mentioned, contrary to the remarks of Muller[37]. The subsequent paper by Wise and Dodge includes a description of how trivalent chromium was oxidized electrolytically to the hexavalent form[39].

The electrolytic regeneration of chromic acid was discussed in some detail by McKee and Leo[40]. The cell in which the oxidation took place utilized a diaphragm to isolate the anolyte in order to keep the cathode from reducing the hexavalent chromium. Best results were obtained with the temperature at 70 F. Lead electrodes were used and the starting electrolyte was essentially a sulfuric acid solution of trivalent chromium. The current efficiency was 59 percent and the authors judge the process to be economically feasible.

Mitter and Dighe[41] reported a process for recovering dichromate and sulfuric acid from the waste pickle liquor used to pickle coinage metal. Again, a diaphragm cell was used. Initially the current efficiency was 90 percent but after 8 hours had dropped to 40 percent.

Descriptions of the commercial methods for producing chromium compounds were reviewed for relevant processing information[7]. In one method, sodium chromate is prepared by first roasting chrome ore with sodium carbonate or sodium carbonate and lime. The chromate is then leached from the mix with water. Chrome ore contains chromium in the form of Cr_2O_3 and the waste sludges under investigation contain hydrated Cr_2O_3 so that the similarity is apparent. Chromium trioxide (CrO_3), orchromic anhydride as it is also called, is prepared by reacting dichromate with sulfuric acid (66 Be or 96 w/o). The temperature is gradually raised to just above the melting point of CrO_3. The mixture separates into an upper layer of predominantly sodium bisulfate and a lower layer of molten CrO_3.

The Bureau of Mines has been active in waste reclamation for some years. Several publications relating to plating wastes have appeared recently. Three of these[42, 43, 44] are concerned with electroplating wastes. The initial work was carried out on HNO_3 rack-stripping solution. The solution was neutralized with lime to pH 2.3-2.7, causing precipitation of ferric hydroxide which contained small amounts of copper and nickel. After precipitation of iron, the copper was reclaimed by controlled cathode potential electrolysis. The nickel was recovered by precipitation as nickel hydroxide, or treated with sulfuric acid and heated to 100 C to expel the HNO_3 and precipitate $CaSO_4$ after which it was recycled as $NiSO_4$ to the nickel plating bath.

An organic-cyanide stripping solution also was used and collected as waste. It was found technically economically feasible to accomplish the neutralization by adding nitric acid waste to the organic-cyanide waste. The metals precipitated at pH 4.5 as cyanides. This method is called the "waste-plus-waste" method. The precipitate was heated in air at 250 C to convert the cyanides to oxides which were leached with 10 percent sulfuric acid. The iron was then precipitated with lime, and the procedure used above was then followed to reclaim copper and nickel values.

The Bureau of Mines have also studied reclamation of aluminum-bearing electronic scrap[45]. Two methods were described. In the first the aluminum was separated by a sodium hydroxide leach with the copper eventually being recovered electrolytically. A precious metal sludge formed during the electrowinning of copper and the precious metals were recovered by conventional means. In a second method, the aluminum was separated by fused salt electrolysis and the copper and precious metals recovered as in the first method.

Two publications[46, 47] by Bureau of Mines personnel describe techniques in the chemical reclaiming of superalloy scrap. Of interest to this project was the method for separating chromium and nickel. Prior to the chromium-nickel separation, liquid-liquid ion exchange techniques were used to extract cobalt, and the chromium and nickel were contained in the acidic raffinate from this separation. Chromium basic sulfate was selectively precipitated using sodium sulfate, sodium carbonate, and urea. The chromium precipitate was contaminated with sodium sulfate so the precipitate was redissolved in sulfuric acid. The chromium was reprecipitated with soda ash, yielding a basic sulfate considered suitable as a leather tanning agent.

Finally, the nickel was precipitated from the chromium-free leach liquor as basic carbonate by addition of soda ash to pH 8. The precipitate was filtered, thoroughly washed, dried, and roasted to give a steelmaking grade of NiO containing 77 percent nickel (the stoichiometric quantity is 78.6 percent). Another method which combines liquid-liquid extraction and electrowinning to reclaim copper and nickel is described in reference (47a).

References (18, (20), (21), and (22) provided data on electrowinning. Reference (18) contained detailed data on the methods used in electrowinning of copper, nickel, and chromium. Copper, because of its noble character, can be deposited from most solutions; nickel is more difficult to reduce electrolytically; and the deposition of chromium from solutions of trivalent chromium is the most difficult of the three. Although electrowinning of chromium has been successful, a high degree of control is required and, in general, results can be erratic. Information also was obtained from the above four references on the other three base metals which are commonly electrodeposited.

Anodic Oxidation

In reference (40) McKee and Leo described an electrolytic process for regenerating reduced solutions of chromic acid. By using a diaphragm cell Cr^{+3} can be oxidized to Cr^{+6} using a lead anode and a current density of 12 amps/sq ft in a sulfuric acid solution at 70 F. McKee and Leo reported an anode efficiency of 59 percent. In experiments for this project similar efficiencies were obtained. About three kilowatt hours are required to produce a pound of CrO_3.

When zinc is present and the chromium is anodically oxidated in acid solution, zinc chromate, an insoluble compound, is formed. Zinc dichromate, on the other hand, is soluble.

One of the easiest and cheapest methods for separating copper from an acid leach solution is cementation. In this process copper is displaced from the solution by metallic iron according to the following equation

$$Cu^{++} + Fe^{o} \longrightarrow Fe^{++} + Cu^{o}.$$

Attesting to the low cost of such an operation is the fact that at Inspiration Consolidated Copper Company as much as 1,000,000 pounds of cement copper have been produced per month with one craneman and three laborers per shift, working two shifts per day[48]. The process removes 97 to 98 percent of the copper.

Habashi[50] in his chapter on precipitation by metals also discusses the conditions for cementing of copper on iron. In addition, he refers to several works on precipitation of cadmium or nickel by zinc.

Electrowinning or other means for reclaiming the metal values from mixed sludges cannot be used until the sludge is solubilized. In the minerals industries the leaching of metal values from ores is an extensively used process. Information on various leaching agents and the chemistry of leaching was also reviewed (48, 49, 50). The ideal leaching agents would be those which were highly selective to individual metals and, therefore, would make for easy separation of the compounds in sludge. Such leaching agents were not found in the literature. Sulfuric or hydrochloric acids are low in cost and would dissolve any of the hydrated oxides. Hydrochloric acid has the disadvantage of being very corrosive which makes it difficult to find suitable materials of construction that are not overly expensive. Neither of the acids is selective. Ammonium carbonate and other ammonium salts have good leaching qualities. The use of additional ammonia with these salts

may or may not be desirable. In some cases in extractive metallurgy more than one leach is necessary to get all the metal into solution. Agitation, temperature, time, and the particle size of the solid material are of importance.

In recent years liquid-liquid extraction, or liquid ion exchange as it is also called, has been studied for use in extractive metallurgy. The technique has been successful for the recovery of uranium and thorium for nuclear applications. Refractory metals such as zirconium and throium also have been recovered by liquid ion exchange techniques. The literature on this technique is very extensive and the research has included just about all metals. Not all of these, however, have found commercial application.

Several excellent review papers were found (51, 52, 53, 54). Many different organic compounds have been used for liquid extraction. The papers of Fletcher and Associates, using naphthenic acid seemed directly applicable to this work. Their numerous publications (55, 56, 57, 58, 59, 60) provided information used to guide the experimental work in this program.

APPENDIX B

DETAILS OF PLANT SURVEY QUESTIONNAIRE

(1) Do you accumulate waste sludge from your metal finishing operation?

( ) Yes ( ) No

(2) Is this sludge the result of controlled neutralization, in a special treatment setup, of waste rinse waters and/or neutralization of spent plating solutions?

( ) Yes ( ) No

(3) Is this sludge the result of uncontrolled neutralization of waste rinse waters and/or neutralization of spent plating solutions? (Example-allowing cleaner rinse to neutralize acidic rinse water from plating baths)

( ) Yes ( ) No

(4) If you do not have a treatment plant for neutralizing waste water and handling sludge, are you planning to install one in the near future?

( ) Yes ( ) No

(5) Has there been any activity in your locality on the part of local, state, or federal agencies to require waste-water treatment?

( ) Yes ( ) No

(6) What is the approximate volume or estimated weight of sludge that you accumulate in a year?

(7) How do you now dispose of your sludge?

( ) Public landfill or dump

( ) Private landfill or dump

( ) Sell to private firm for reclamation

(8) Do you make or have you ever made an attempt to reclaim metal values from the sludge?

( ) Yes ( ) No

(9) What metals might be found in your sludge?

( ) Copper	( ) Zinc	( ) Precious metals (specify)
( ) Nickel	( ) Cadmium	
( ) Chromium	( ) Tin	( ) Others (specify)

(10) Would you be willing to cooperate in the MFF--sponsored project by allowing Battelle personnel to take sludge samples from your plant?

( ) Yes ( ) No

(11) If the answer to question 10 is yes, please give name of person to be contacted.

(12) Please give the name, address, and telephone number of your company.

Upon completion of this questionnaire, please return to:

Arch B. Tripler, Jr.
Waste Control and Process Technology Division
Battelle Memorial Institute
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

APPENDIX C

DETAILS OF FIELD STUDIES: PLANT VISITATIONS AND SLUDGE CHARACTERISTICS; SLUDGE WEATHERING AND LEACHING

Company A. This company has more than one plant. The one from which the sludge samples were obtained plates copper, nickel, and chromium on plastics. No cyanide solutions are used. The facility in which wastewaters are treated is automatically controlled. The hexavalent chromium is reduced with bisulfite and then trivalent chromium, copper, and nickel are precipitated as hydroxides by raising the pH to about 8 with sodium hydroxide. In the past lime had been used in neutralization to promote flocculation and some calcium is still found in the sludge lagoons. The hydroxide slurry is pumped to a clarifier, and finally to one of two cement- and block-lined lagoons. The settled slugde is removed from the lagoon and hauled to a municipal landfill. The water going into the sewer contains no dissolved solids in excess of local standards. Some tin is found in the sludge because in making the plastic surface conductive, a very thin tin-palladium layer is deposited, with the tin being subsequently stripped. The sludge in the lagoon was very "clean", that is, it looked uniform and free of extraneous materials.

Company B. At this facility sludge is collected in a sump and sludge formation depends on chance neutralization as acid and alkaline wastewaters are brought together. Precipitation probably is not complete, allowing some of the dissolved metals to pass to the sewer. It is suspected that the sump is not efficient in retaining all the precipitate and some of the sludge also passes to the sewer. The resultant wastewater passing to the sewer may be alkaline or acid depending on which of the wastewaters was in excess.

Copper, nickel, chromium, zinc, tin, and cadmium are plated at Company B. Phosphating is also done. The sludge had oil, grease, and other extraneous matter mixed with it and, judging from the variations in color, the sludge was segregated within the sump. The sump is periodically pumped out and the sludge hauled to a dump for disposal.

Company C. The sludge at Company C also is collected in a sump. Just as at Company B, the acid and alkaline wastes are mixed, with neutralization occurring and the resultant wastewater being acid or alkaline depending on which was in excess at the time of mixing. Copper, nickel, chromium, cadmium, and silver are plated. Some metal surfaces are phosphated and aluminum is etched. The sludge appears to be even more

highly segregated than that from Company B. The sludge contains extraneous material such as cloth, wood, paper, and oil or grease. When the sump is filled, the sludge is pumped out and hauled to a dump.

Company D. This company anodizes aluminum and the sludge that is collected precipitates from the alkaline solution used to etch the aluminum prior to anodizing. This sludge is separated from the wastewater by a rotary vacuum filter. Presumably the sludge is largely sodium aluminate, $AL(OH)_3$.

Company E. Copper, nickel, chromium, zinc, and cadmium are plated at Company E. This plant treats its wastewater by reducing hexavalent chromium to the trivalent state using SO_2 or bisulfite, and destroying cyanide completely in two stages with the alkaline chlorine treatment. The metals are precipitated as hydroxides with NaOH or CaO. The sludge goes to a settling tank and then to the earthen lagoon. The sludge appeared segregated and samples were taken from several places.

Collection of sludge at this plant was started only a short time prior to our sampling. It is estimated that about 25,000 pounds will be collected per year. No arrangement had been made for its disposal.

Company F. This company has been accumulating sludge for 10 to 11 years in a storage lagoon. Because of this relatively long storage period, the lagoon was of interest for the study of "weathering" effects on solubility and leaching.

The metals which are found in the wastewaters get there largely as a result of the pickling of brass, copper, and bronze. Hence, one would expect copper, zinc, and tin in addition to chromium. Hexavalent chromium plays a large part in this process and part of the waste treatment consists of reducing this hexavalent chromium to the trivalent state. The metals are precipitated as hydroxides by addition of lime. The stream passes through a series of settling tanks and finally arrives at the holding lagoons where final settling occurs, and also, some natural dewatering. When the sludge reaches a certain stage of dryness, it is transferred to the storage lagoon.

Company G. Company G does copper, chromium, cadmium, and zinc plating. Wastewaters are treated to reduce chromium and to destroy cyanide completely. After some settling the sludge flows by gravity to a lagoon where further settling takes place. The supernatant liquid is then run

by gravity to a second lagoon where any suspended matter is permitted to settle. Finally, the supernatant liquid from the second lagoon goes to a nearby stream. The sludge was taken from the first lagoon and appeared segregated so samples were taken at several places. Dewatering is not nearly so efficient as with Company F sludge.

Sludge Characteristics

Determination of the amount of water in a given sludge is difficult because the sludge concentration varies with depth due to settling; the storage lagoons vary in depth, and the dense layer of settled sludge varies in thickness, being thickest at the point where sludge enters the lagoon. The samples for use in this work were taken at several spots in a given lagoon if possible. A stainless steel conical, 1/2-gallon sampler was plunged into the sludge layer which was usually 2 to 3 feet below the top surface of the liquid, held a few seconds and withdrawn. The samples were vacuum filtered using a Whatman No. 2 paper, and after all the solids were in the Buchner funnel, the vacuum was maintained until no visible water passed through the funnel for a period of three minutes. This was arbitrary but it did provide a uniform basis for filtration. The sludges filtered fairly easily. Dried samples were prepared by heating the filter cake to 200 F for several hours. Semi-quantitative spectrographic analyses were made of these dried samples.

Company A. The first batch of sludge obtained from this company was rather "thin"; that is, the percent solids was low, being about 1.6 percent of the slurry as sampled. The second batch obtained was much thicker and contained at least 4 percent solids. However, these figures are semi-quantitative because uniform sampling is not possible.

The filter cake from the first batch contained 87 percent water, and from the second batch about 80 percent water. Even with 87 percent water the filter cake can be added to the leaching agent and little dilution occurs.

Companies B and C. The sludges from these companies were very much alike in that they contained organic material. This organic material appeared to be partly grease and oil and would be expected to coat sludge particles and prevent contact with leaching agents. Dried samples of each were incinerated, and it was observed that Sludge B burned autogeneously once it had started to burn. Sludge C did not burn autogeneously. The gross heating values of dried samples of Sludges B and C were measured calorimetrically as 2155 Btu/lb, and 1170 Btu/lb, respectively.

The solids contents of these samples were about the same as for the second sample of Sludge A, that is, about 4 percent.

Company D. The "as received" sludge from Company D was moist filter cake from the vacuum filtration. It contained 32 percent solids. The sludge contained about 10 percent aluminum and 10 percent silicon. Petrographic examination of an incinerated sample showed a fairly large amount of diatomaceous filter aid material present. Filter aid was used on the rotary vacuum filter.

Little further work was done with this sludge because it appeared unlikely that the aluminum could be profitably recovered.

Company E. The solids content of the sludge samples "as taken" averaged 2.7 percent. The filter cake obtained by the standard method described above from two samples contained 13 percent and 11.4 percent solids, respectively. The filter cake had a yellowish green color.

Company F. The sludge from Company F was quite dry in the "as taken" condition. In taking the samples one could walk on the surface of the sludge in the storage lagoon. For three samples the solids contents were 41.7 percent, 36.5 percent, and 43.5 percent, respectively. The solids contents here were higher than those obtained from filter cakes of previously described "wet" sludges. This is an indication of the efficiency of "air and solar" dewatering obtained by the sludge handling system at Company F.

Company G. Two samples of "as sampled" sludge from Company G contained 3 percent and 3.9 percent solids. The moist filter cake contained 16 percent solids. The overall color of one sample was brown with spots of bluish-green and yellow, while a second sample appeared blue-green with spots of yellow-brown. The sludge appeared highly segregated. The first sample was taken near the entry pipe and the second was taken farther away.

Sludge Weathering and Leaching

A schematic diagram of the locations of the three core drillings and the results of a gross examination of the structures just beneath the sludge bed are shown in Figure C-1. At the indicated locations, casings were driven down through the sludge into the shale formation beneath the sludge bed. The sludge cores were taken from within these casings.

For all three sludge cores, two sludge samples were taken from within the 1-foot segment of the sludge cores. An extra sludge sample was taken from the 4 to 5 foot segment of core B-1, making a total of three samples for this segment of this core.

After all the sludge had been removed from within the casings, the underlying shale structure was cored. The core drill was dropped through the now-empty casings to ensure that the shale cores were not contaminated by the sludge.

The sludge samples were placed in glass jars, the shale cores in special wooden cases; then the entire lot was shipped to Battelle's Columbus Laboratories.

Figure C-1 indicates the degree of recovery of the shale cores. Less than complete recovery was obtained where the shale formation was partly or completely decomposed, or where siltstone was encountered.

Two shale core samples from each of the three bore holes were selected for analysis. The samples represented the portion of the core from immediately below the sludge bed and the portion at the bottom of the bore hole. Analyses were also made on sludge samples taken from as near the bottom of the sludge bed as possible. There was not a clear demarcation where the sludge stopped and the shale began. This is probably due to the fact that there was loose shale left at the bottom of the lagoon prior to adding the first load of sludge. Therefore, those sludge samples were selected which, upon visual inspection, had no shale present.

The six core samples were first crushed in a jaw-crusher, then in a roll crusher, and finally in a pulverizer. The powdered samples were rolled in a roll mixer for several hours and small samples were taken for analysis. The three sludge samples were dried, ground, thoroughly mixed, and sampled.

Table C-1 shows the results of the semi-quantitative spectrographic analyses.

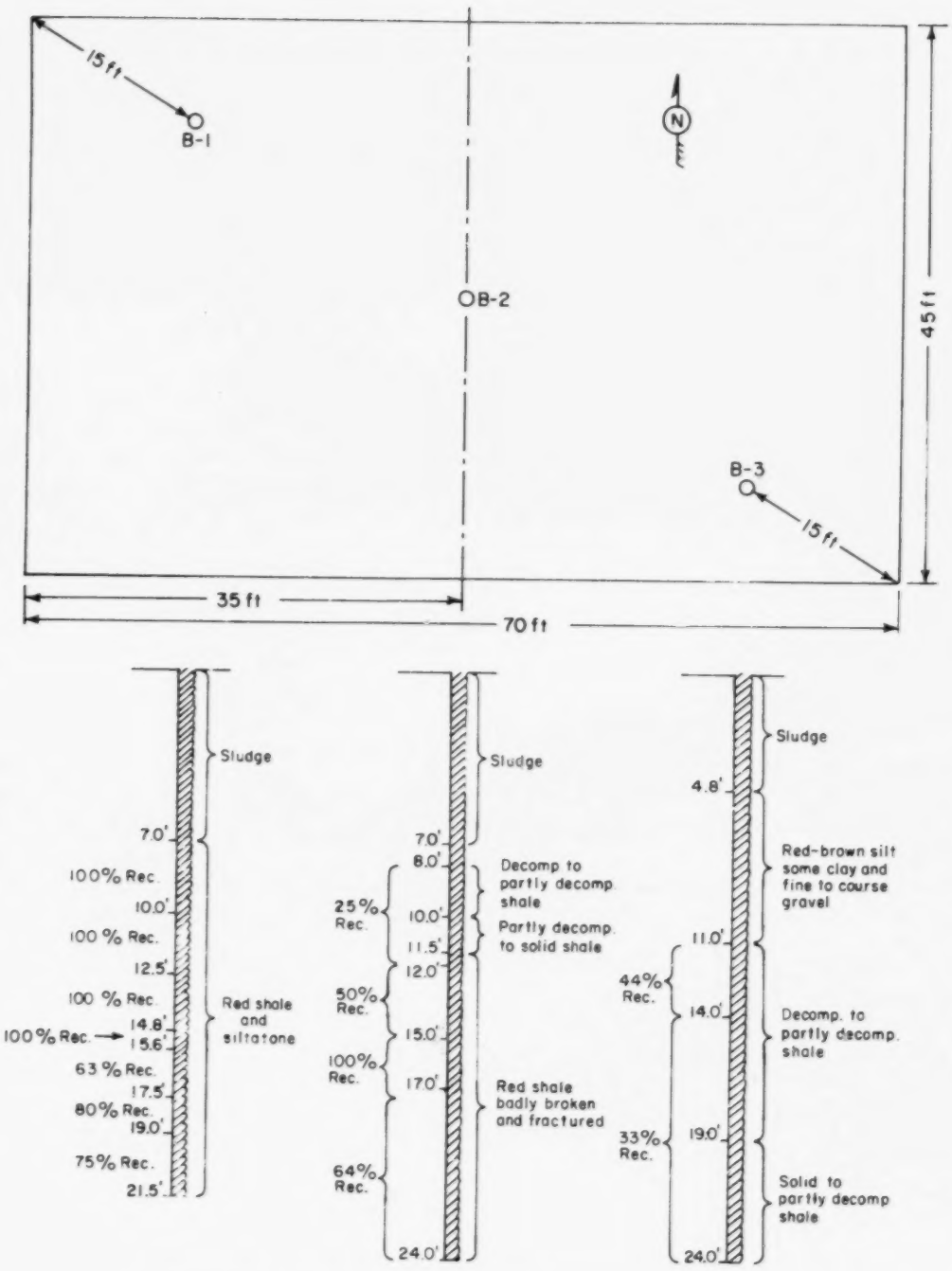


Figure C-1. Schematic drawing of location of bore-holes, results of gross examination of cores, and percentage recovery of cores

Table C-1. SEMI-QUANTITATIVE SPECTROGRAPHIC ANALYSIS OF SELECTED SLUDGE AND CORE-DRILLING SAMPLES

SAMPLE NUMBER	Sludge No. 13	Core A-1	Core t-2	Sludge No. 13	Core A-1	Core D-3	Sludge No. 13	Core A-1	Core B-2
Bore Hole	B-1	B-1	B-1	B-2	B-2	B-2	B-3	B-3	B-3
Approximate Depth	5'8"-6'0"	7'0"-7'9"	19'9"-21'6"	6'6"-7'0"	8'0"-12'0"	23'1"-24'0"	3'6"-4'0"	11'0"-14'0"	19'0"-24'0"
Weight Percent (a)									
Cu	2.-4.	.005	.005	2.-4.	.005	.005	3.-6.	0.01	0.005
Ni	0.1	.005	0.01	0.3	0.005	<0.005	0.8	<0.005	<0.005
Cr	5.-15.	<0.01	0.02	5.-10.	<0.01	<0.01	5.-15.	<0.01	<0.01
Zn	0.2	0.1	<0.1	0.3	<0.01	<0.1	2.	<0.1	<0.1
Fe	0.5	3.-6.	3.-6.	0.7	3.-6.	3.-6.	0.7	3.-6.	3.-6.
Ca	5.-10.	2.	1.	5.-15.	0.5	5.	5.-10.	0.5	4.
Sn	0.2	<0.01	<0.01	0.2	<0.01	<0.01	0.4	<0.01	0.01
Ba	<0.01	0.03	0.03	<0.01	0.03	0.03	<0.01	0.03	0.03
S	0.01	0.02	0.02	0.01	0.02	0.01	0.02	0.01	0.02
Si	2.-4.	10.-20.	10.-20.	2.-4.	10.-20.	10.-20.	3.-5.	10.-20.	10.-20.
Mn	<0.01	0.05	0.03	<0.01	0.05	0.1	<0.01	0.1	0.1
Mg	0.3	2.	2.	0.4	2.	2.	0.6	1.	2.
Al	2.	5.-15.	5.-15.	2.	5.-15.	5.-15.	3.	5.-15.	5.-15.
Mo	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01
Na	0.1	2.	2.	0.1	2.	3.	0.1	3.	2.
V	--	0.01	0.01	--	0.01	0.01	--	0.01	0.01
Ti	0.05	0.3	0.3	0.1	0.3	0.3	0.1	0.3	0.3
Zr	<0.01	0.01	0.01	<0.01	0.01	0.01	<0.01	0.01	0.01
Pb	0.05	--	--	0.04	--	--	0.08	--	--
Ag	<0.005	--	--	<0.005	--	--	<0.005	--	--

(a) Accuracy ± 50 percent.

APPENDIX D

DETAILS OF LABORATORY STUDIES, LEACHING EXPERIMENTS, LIQUID ION EXCHANGE

Leaching Experiments

For the most part, leaching experiments were made on dried sludge. (Doing this made possible quantitative experiments, because with filter cake there were variations in moisture content. However, in a commercial process filter cake would be used.) Some selectivity was shown by ammonium carbonate solutions where chromium compounds remained largely undissolved while nickel and copper compounds were solubilized. Sulfuric acid solutions left calcium sulfate undissolved but did not differentiate between the heavy compounds.

Because the sludges showed individual leaching characteristics, they are discussed below on an individual basis.

The conditions and results of the leaching tests are given in Table D-1.

Company A Sludge

Sludge from Company A was, for a time during the early stages of this project, the only suitable sludge available. It contained only three heavy metals in significant quantities, and it was very clean, having neither grease nor oil nor other gross impurities.

The undissolved material consisted mostly of $CaSO_4$. The difference in the percentage dissolved between experiments 2 and 3 is attributed to difference in agitation.

When Sludge A was incinerated at 1200 F it lost 25 percent of its weight. This is mostly due to water loss. Drying sludge at 200 F does not rid the hydrated oxides of all the water. Incinerating also oxidizes part of the insoluble trivalent chromium to soluble hexavalent chromium. If incineration is used to reduce volume prior to dumping, then the hexavalent chromium can leach out and find its way into the ground water. This was discussed in reference (26). The concentration of reclaimable metals is higher in the incinerated sludge and this is an advantage because where leaching follows incineration less material handling is required. The higher concentration of metal values is reflected in the smaller amount dissolved in experiment 4.

Table D-1 SELECTED LEACHING EXPERIMENTS

Run No.	Sludge	Condition	Wt. gm.	Leachant	Vol. ml.	Temp. F.	Time hrs.
1	A	Dried	25.0	1:1 H_2SO_4	100	170	16
2	A	Dried	25.0	1:1 H_2SO_4	150	170	11-1/4
3	A	Dried	25.0	1:1 H_2SO_4	150	170	11-1/4
4	A	Incinerated	10.0	1:1 H_2SO_4	150	150	1-1/2
5	A	Dried	100.0	30% H_2SO_4	1000	145	16-3/4
15	B	Incinerated	20.0	1:1 H_2SO_4	75	180	14-1/2
15a	B	(Residue from above)	12.9	1:1 H_2SO_4	75	195	21
16	C	Incinerated	20.0	1:1 H_2SO_4	75	180	14-1/2
16a	C	(Residue from above)	17.8	1:1 H_2SO_4	75	190	21
23	E-1	Dried	10.0	1:1 H_2SO_4	100	70	4-1/2
24	E-2	Dried	10.0	1:1 H_2SO_4	100	150	3-1/4
30	F-1	Dried	10.0	1:1 H_2SO_4	150	150	1-1/2
31	F-2	Dried	10.0	1:1 H_2SO_4	150	150	1-1/2
35	F-4	Dried	10.0	1:1 H_2SO_4	150	150	1-1/2
36	F-5	Dried	10.0	1:1 H_2SO_4	150	150	1-1/2
5	A	Dried	100.0	30% H_2SO_4	1000	145	16-3/4
6	F-1	Dried	10.0	20% H_2SO_4	100	75	24
8	F-1	Dried	10.0	20% H_2SO_4	100	75	24
7	A	Dried	10.0	30% $(NH_4)_2CO_3$	200	175	5-2/3
7a	A	(Residue from above)	8.5	30% $(NH_4)_2CO_3$	200	175	9
7b	A	(Residue from above)	7.3	30% $(NH_4)_2CO_3$	200	175	6-1/2
7d	A	(Residue from above)	7.0	1:1 H_2SO_4	100	175	7-1/2
10	A	Dried	10.0	70% $(NH_4)_2CO_3$	200	70	108
11	A	Dried	10.0	65% $(NH_4)_2CO_3$	200	70	71
11a	A	(Residue from above)	9.4	65% $(NH_4)_2CO_3$	200	70	22
11b	A	(Residue from above)	9.0	65% $(NH_4)_2CO_3$	200	70	24
12	A	(Residue from above)	5.0	1:1 H_2SO_4	175	140	17-1/2
14	A	Incinerated	5.0	20% $(NH_4)_2CO_3$	100	150	1-1/2
17	E	Dried	15.0	30% $(NH_4)_2CO_3$	200	130	6-1/4
18	E	Incinerated	15.0	30% $(NH_4)_2CO_3$	200	150	6-1/4
17	A	Dried	15.0	30% $(NH_4)_2CO_3$	200	150	6-1/4
19	A	Incinerated	15.0	30% $(NH_4)_2CO_3$	200	130	6-1/4
28	E-1	Dried	10.0	65% $(NH_4)_2CO_3$	200	70	69
28a	E-1	(Residue from above)	8.8	65% $(NH_4)_2CO_3$	200	70	24
28b	E-1	(Residue from above)	6.8	65% $(NH_4)_2CO_3$	200	70	64
11	A	Dried	10.0	30% $(NH_4)_2CO_3$	200	70	24
11c	A	(Residue from above)	9.7	1:1 H_2SO_4	175	70	24
17	A	Dried	10.0	14% $(NH_4)_2CO_3$	200	200	23
17	E-1	2% Na_2CO_3 Dried	10.0	23% $(NH_4)_2CO_3$ + 2% Na_2CO_3		150	4
17a	(Residue)	2% $NaOH$ Dried	9.6	23% $(NH_4)_2CO_3$ + 2% Na_2CO_3		150	4
27	E-2	Dried	10.0	30% $(NH_4)_2CO_3$	200	70	69
27a	E-2	(Residue from above)	7.4	30% $(NH_4)_2CO_3$	200	70	24
27b	E-2	(Residue from above)	6.7	30% $(NH_4)_2CO_3$	200	70	6.7
9	A	Dried	10.0	20% NH_4Cl	200	175	5-2/3
9a	A	(Residue from above)	7.3	20% NH_4Cl	200	175	9
9b	A	(Residue from above)	6.6	20% NH_4Cl	200	175	6-1/2
9d	A	(Residue from above)	5.0	1:1 H_2SO_4	100	175	7-1/2
9	A	Dried	10.0	20% $(NH_4)_2SO_4$	200	175	5-2/3
9a	A	(Residue from above)	9.2	20% $(NH_4)_2SO_4$	200	175	9
9c	A	(Residue from above)	7.8	20% $(NH_4)_2SO_4$	200	175	6-1/2
9d	A	(Residue from above)	5.0	1:1 H_2SO_4	100	175	7-1/2
21	D	Incinerated	5.0	1:1 HCl	100	150	3
22	D	Incinerated	15.0	1:1 HCl	300	150	3
33	E-3	Dried	10.0	25% NaOH	100	150	2
33a	E-3	(Residue from above)	6.8	1:1 H_2SO_4	50	140	1
34	E-3	Dried	50	25% NaOH	150	150	1
34a	E-3	(Residue from above)	50	1:1 H_2SO_4	150	140	1
42	E-1	Dried	10.0	7% $(NH_4)_2CO_3$	125	75	2

Table D-1. SELECTED LEACHING EXPERIMENTS (Continued)

Leach Solution Cu g/l	Cr g/l	Ni g/l	Residue Properties Wt. gms.	% Cu	% Cr	% Ni	Extraction % Cu	% Cr	% Ni	% Wt.	Remarks
1:1 H_2SO_4 Leaching											
			8.1							67.6	
			9.9							60.4	
			8.3							67.0	
			5.0							50.0	
			30.2							69.8	
			12.9							36.4	
			12.0							40.0	
			17.8							11.0	
			17.4							13.0	
			5.0							50.4	
			7.0							30.2	
			4.8							51.6	
			5.3							47.1	
			4.0							61.0	
			6.0							40.0	
			Dilute H_2SO_4								
			30.2							69.8	
			9.9							1	
			6.0							40	
$(NH_4)_2CO_3$ Leaching											
			7.8							21.6	
			7.3							26.9	
			ND							ND	
			3.1							69.0	
			7.7							22.3	
			6.6							34.3	
			5.6							43.8	
			5.0							50.0	
			3.0							70.3	
			4.0							20.0	
			12.75							17.5	
			13.0							13.2	
			13.8							7.9	
			15.0							0	
			7.9							21.3	
			6.8							32.5	
			7.3							36.3	
Insert in $(NH_4)_2CO_3$ in proper sequence											
			7.7							22.3	
			3.0							70.3	
Modified $(NH_4)_2CO_3$ Leaching											
			8.6							23.3	
			8.0							20.1	
			8.8							31.8	
Insert in $(NH_4)_2CO_3$ Leaching in proper sequence											
			4							25.8	
			6.7							32.5	
			5.4							36.3	
(Ammonium Salt Leaching)											
			7.5							23.4	
			6.6							36.5	
			ND							ND	
			0.2							97.5	
			9.7							2.8	
			7.9							21.4	
			ND							ND	
			0.2							97.5	
NCl Leaching											
			5.8							42.0	
			6.3							36.6	
NaOH Leaching											
			6.8							32.0	
			1.5							85.0	
			ND							ND	
			1.1							86.4	
Put in proper place in $(NH_4)_2CO_3$ Leaching											
			8.4							6.3	

Although very concentrated sulfuric acid solutions were used initially, hopefully to speed up leaching, it is advisable for economic reasons to use a more dilute acid solution. In experiment 5, 20 w/o (weight percent) sulfuric acid solution was used with good results. Ten or twenty percent solutions would do for commercial processing.

Hydrochloric acid is very efficient, dissolving 98 percent of sludge A. The calcium goes into solution, accounting for the increase compared to sulfuric acid leaching. Hydrochloric acid is very corrosive and gives rise to toxic fumes and in addition to its lack of selectivity, these disadvantages have given rise to some hesitancy in using it as a leachant.

Ammonium carbonate has been used as a leachant for many years in extractive metallurgy with good results. In experiments 7 through 9, ammonium carbonate, ammonium chloride, and ammonium sulfate were used at 175 G. Three successive leaches were used and finally the undissolved residue was treated with sulfuric acid. Considering the first two leaches, the chloride is more efficient, with the carbonate being next. The chloride and the sulfate will tend to act similarly to HCl and H_2SO_4. Calcium should remain as an insoluble carbonate in ammonium carbonate solution but some calcium may dissolve as the bicarbonate. Ammonium carbonate does not take the chromium into solution. The chromium from Sludge A settled out of the carbonate solution as a violet precipitate. An experiment (28575-55) in which an attempt was made to dissolve hydrated chromium trioxide (present alone) in ammonium carbonate failed. This selectivity makes possible the separation of one metal during leaching.

Ammonium carbonate solutions at elevated temperatures tend to lose some ammonia. Two experiments (10 and 11) at room temperature demonstrated that with an increase in the time leaching efficiency was about the same. The time need not be as long as in experiment 10 (7 days). Supplementary additions of ammonia are often used in ammonium carbonate solution and this was tried in experiment 12. A slight increase in the amount dissolved was effected but this could have been due to the longer time. An increase in the ammonium carbonate concentration from 200 g/l to 350 g/l did result in an increase in the amount of sludge dissolved (experiment 13). Based on experience with dried sludge, incinerated Sludge A dissolved to about the extent expected in ammonium carbonate solution.

The major principles demonstrated by these experiments are that the advantage of sulfuric acid as a leaching agent is that dissolution of copper, nickel, and chromium compounds is completed in a single treatment, and that ammonium carbonate leaching has the advantage that chromium is not dissolved, i.e., ammonium carbonate is somewhat selective.

Company B and Company C Sludges

It will be recalled that Companies B and C did not treat their wastewater to obtain sludge. All waste streams ran into a common sump where neutralization or precipitation was uncontrolled. In addition, both sludges contained considerable organic material and some sulfides. Upon treatment with acid, H_2S was given off from dried sludge samples. No H_2S evolved from the incinerated sludge on treatment with acid. In general, the leaching with sulfuric acid or ammonium carbonate resulted in less dissolution than with Sludge A. Data on experiments 15 through 19, Table D-1, give information on the leaching behavior of these sludges. These sludges were not used for reclamation experiments because more suitable sludges were available.

Company D Sludge

The sludge from Company D originated from caustic etching of aluminum and aluminum alloys. About 40 percent of the incinerated sludge was soluble in 1-1 hydrochloric acid. The resulting solution was yellow and tests for trivalent iron were positive. Recovery of aluminum was judged to be uneconomical. The incinerated sludge could be used for landfill, or for some application in the ceramic industry.

Company E Sludge

Two samples of sludge were taken from the lagoon at Company E, one close to the inlet (E1) and the second away from the inlet (E2). Dried portions of these samples were leached with sulfuric acid, ammonium carbonate, and sodium hydroxide. Neither sludge dissolved as well as sludge A did in sulfuric acid or ammonium carbonate (experiments 23-27, Table D-1. The reason for this is not known. The only difference in the treatment at the plants was the complete oxidation of cyanide at Company E. Company A used no cyanide baths.

Because Company E sludge contained zinc, an initial leach with 25 w/o NaOH (experiments 27 and 29) was used with the intent of separating the zinc as zincate. However, it was found that chromium dissolved as a chromite and that some copper also dissolved. It was reported in the literature that both chromium and copper will precipitate on boiling the alkaline solution. Experiments showed that the precipitation of chromium and copper was not complete. The caustic leach was eventually

abandoned because of these drawbacks. The residue recovered was then leached with sulfuric acid (experiments 29a and 29b, Table D-1.)

Company F Sludge

Several samples were taken at various places in the sludge storage lagoon. Leaching results with two samples are given here. Again the amount dissolved in sulfuric acid was less than with Sludge A. The behavior in ammonium carbonate was similar to that of Sludge A.

Company G Sludge

This sludge dissolves fairly well in sulfuric acid at elevated temperatures but very slowly in ammonium carbonate (experiments 33-37).

Liquid Ion Exchange

Because results were favorable, considerable effort was given to experiments on the reclamation of metals by solvent extraction (also referred to as liquid-liquid extraction or liquid ion exchange). Because of the current relatively limited application of this technique on a commercial scale, such techniques are not commonly familiar. Therefore, a short description follows.

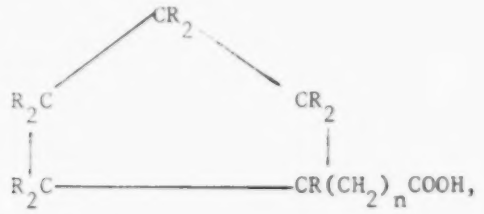
In this method, an aqueous solution of two or more metal ions is agitated vigorously with an organic solvent that is immiscible with water. If conditions, particularly pH, are adjusted correctly, a single metal ion will transfer to the organic phase. In this way the extracted metal ion is selectively separated from other metal ions in the aqueous phase. The pH required for extraction is the pH at which the particular metal hydroxide begins to precipitate (in the aqueous phase).

The metal ion being extracted is distributed in the two phases according to the equation

$$D = \frac{Co}{C_A}$$

where D is the distribution coefficient, Co is the concentration of the metal ion in th organic phase, and C_A is the concentration of the metal ion in the aqueous phase. The higher the value of D the more efficient is the given organic solvent as an extractant.

After the two phases have been separated the organic phase is treated in such a way that the metal ions are stripped from the organic medium and the organic solvent is restored to its original condition (except for the water that it dissolves) and can be recycled. If it is desired to separate a second metal ion from the original aqueous phase, the pH is changed and the aqueous solution is again agitated vigorously with organic solvent. For each metal ion present more than one extraction may be necessary. Many organic solvents have been investigated. It was not possible to study all of these in connection with this project. The first organic agent selected for study is naphthenic acid. The naphthenic acids have the general formula:



where R is hydrogen or an alkyl group.

The reaction between a metal ion, e.g., copper, and naphthenic acid may be expressed as follows:

$$Cu^{++}\ (aq.) + 2\ RCOOH \underset{\text{stripping}}{\overset{\text{extraction}}{\rightleftharpoons}} Cu(RCOO)_2 + 2H^{+}\ (aq.).$$

This is actually a liquid ion-exchange reaction in which hydrogen ions are given up in exchange for copper ions.

The naphthenic acid[1] used for the work here is a mixture of acids rather than a single compound. Prior to extraction the naphthenic acid was dissolved in kerosene to form a 1M solution. The general scheme for separating and electrowinning copper and nickel is shown in Figure D-1. The nephthenic acid solution was added to a sulfuric acid leach solution of sludge F, whose pH had been adjusted to 5.2, the pH for copper extraction. The agitation was done in a 500 ml separatory funnel. Three extractions were made to get all the copper. Sludge F was used in this preliminary work because it had 2-6 percent copper and practically no nickel.

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(1) Chevron Chemical Company, Des Plaines, Illinois, Grade E Naphthenic Acid.

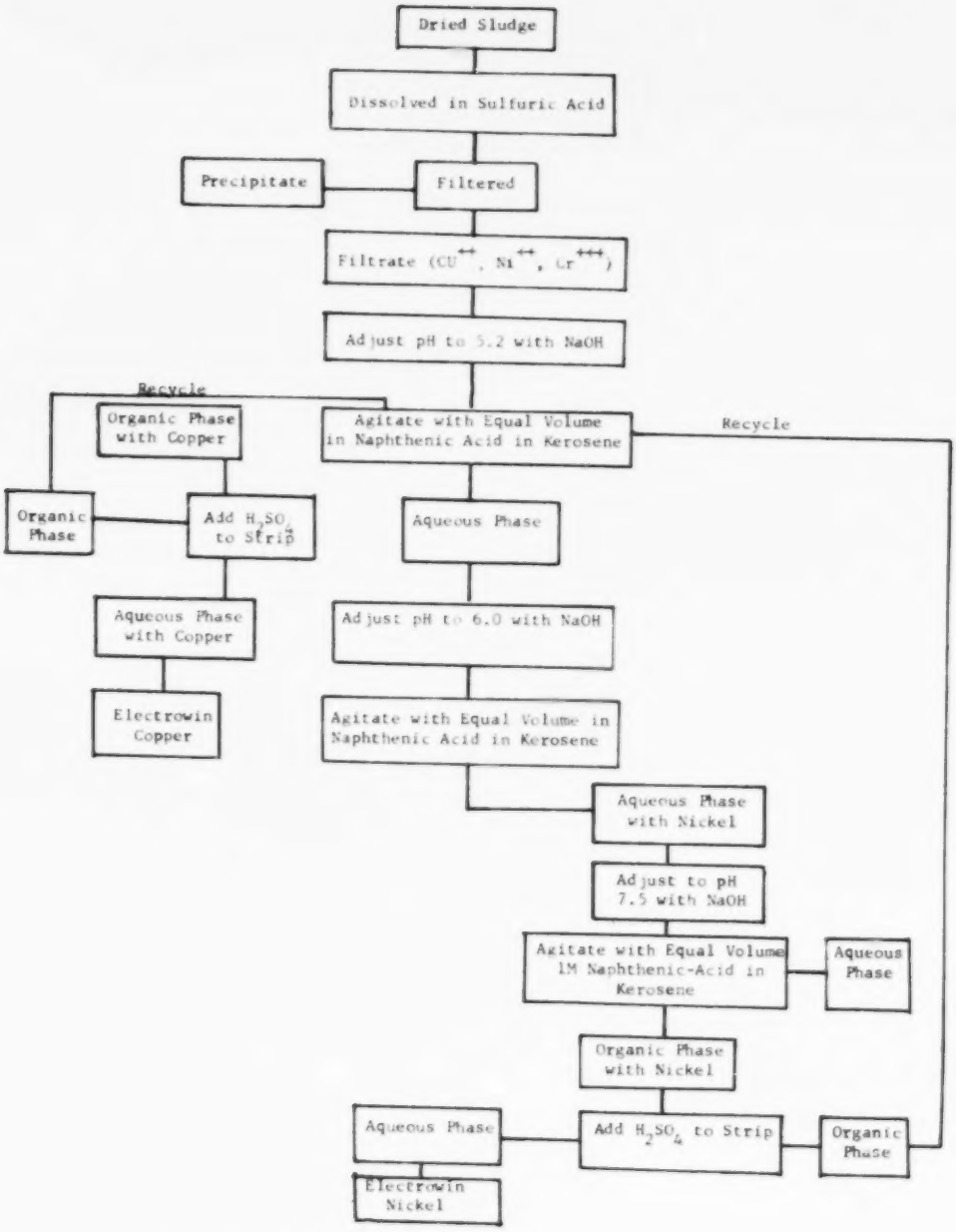

FIGURE D-1. Flow Diagram for Proposed Method for Separating Copper and Nickel Using Naphthenic Acid

A series of thirteen runs were then made using leach liquors prepared from Company A dried sludge. Table D-2 compares the materials used in Runs 7 through 14. Runs 1 through 5 were discontinued before completion for various reasons such as precipitate formation, excessive emulsion problems and loss of part of one or more fractions in the runs.

Figure D-2 shows a generalized flow chart for the liquid-liquid extraction processes used and the nomenclature and code referring to the processing steps. The sample code used in the general form XNYM where X is the run number, N is the process step designation (E for extraction products, R for stripping products, etc.), Y is the extraction step number and M is a letter A, B, C, etc., to show first stripping, 2nd, 3rd, etc. The sample Code 7R3B, for example, means Run Number 7, enriched stripping liquor (R) is that the raffinate from the second (B) strip of the organic fraction from the third (3) extraction step.

In most of the runs, the pH of the leach liquor filtrate was first adjusted to one of four ranges: below 2.5, 2.5 to 4.5 (extraction range for Cu), 5.0 to 7.0 (extraction range for nickel), and above 7.0. A typical run would start by adjusting the leach liquor filtrate to 2.5 to 4.5. This would be followed by filtration if needed. One or more extractions then were made on the adjusted filtrate with naphthenic acid solution, until repeated successive extraction steps no longer significantly reduced the pH of the partially depleted feedstock. The copper was next stripped from the organic phase by treating with dilute H_2SO_4 solution. The pH of the partially depleted feedstock then is adjusted to the 5.0 to 7.0 range or higher, filtered if necessary, and nickel extracted with 100 ml of approximately 1.0 M naphthenic acid in kerosene. The naphthenic acid solution(s) was stripped with 50 ml fractions of 0.5 M H_2SO_4. After one or more strippings, the naphthenic acid solution was recycled into the next extraction step. Repeated extractions were necessary at pH 5 to 7 or higher, if much ammonia was present, since concentrated solutions of ammonium sulfate inhibit the nickel extraction. Extractions were terminated when a spot test of the partially depleted feedstock for nickel showed no nickel or only a trace present.

All runs were made using 500 ml separatory funnels as contacting vessels, with 2 minutes of vigorous agitation (shaking) followed by settling until two separate layers formed and stabilized. Then the denser aqueous phase was drawn off (separated) and further processed according to the specifications of each particular run.

Runs 7, 8, 9, 10, and 12 were made using feedstock from an $(NH_4)_2CO_3$ leach of Company A dried sludge. Fifty grams of the latter were added to 1 liter of ammonia carbonate solution composed of 300 g $(NH_4)_2CO_3$ in distilled water. Leaching was carried out in a 2-liter beaker at 115 to 120 F for 4 hours with stirring. The slurry settled overnight

MATERIALS USED IN LIQUID-LIQUID EXTRACTION RUNS 7 THROUGH 14

Run Number	Initial (ml)	Feedstock (type)[a]	Acids or Bases Added			Extraction Liquor Naphthenic Acid E in Kerosene		Stripping Liquor	Maximum[b] Metals Available for Recovery		
			1:1 H_2SO_4 (ml)	$Ca(OH)_2$ (g)	1:1 NH_4OH (ml)	Acid (g)	Total Volume (ml)	0.5 M H_2SO_4 (ml)	Cu (g)	Ni (g)	Cr (g)
7	92.5	I	21.65	None	2.5	27.5	100	460	0.25	0.25	0.75
8	92.5	I	None	None	None	82.5	300	700	0.25	0.25	0.75
9	92.5	I	5.00	None	None	55.0	200	500	0.25	0.25	0.75
10	92.5	I	10.0	None	None	55.0	200	450	0.25	0.25	0.75
11	95.0	II	None	1.78+[c]	7.9	55.0	200	1300	0.50	0.50	1.50
12	80.0	I	12.0	None	None	100	300	300	0.22	0.22	0.65
13		III	0.42	None	19.2	100	300	400	0.25	0.25	0.75
14	100	IV	2.25	10.0	9.6	100	200	500	0.34	0.34	1.00

(a) I is filtrate from ammonium carbonate leach; II is filtrate from 1:1 H_2SO_4 leach; III is an alkaline ammonium sulfate leach; and IV is also an alkaline ammonium sulfate leach with small amounts of ammonium phosphate and ammonium carbonate added to reduce magnesium and calcium in solution.

(b) Based on the approximate analysis of Company A sludge as reported previously (3-5% Cu, 3-5% Ni, 5-15% Cr).

(c) Amount used during run. More than 30 grams of $Ca(OH)_2$ was used to neutralize the acid leach and adjust the pH to 1.70 for the feedstock.

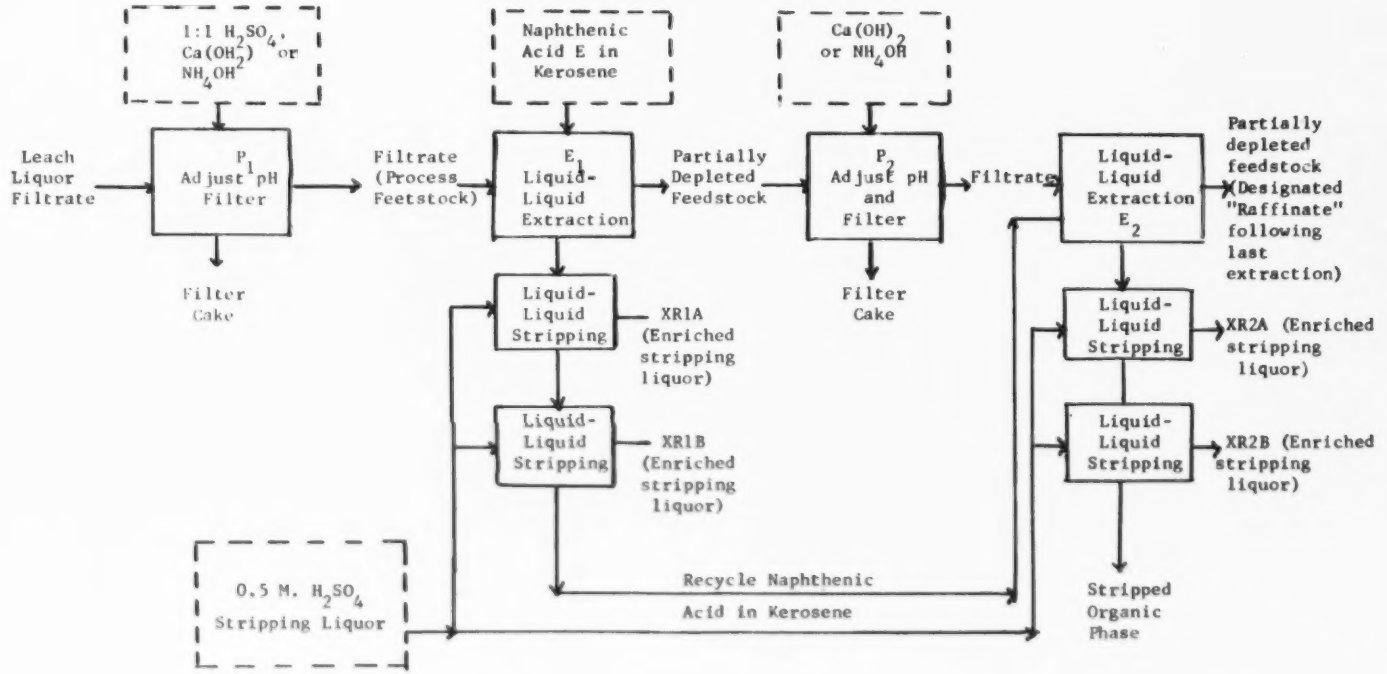

FIGURE D-2. Generalized Flowshart of Liquid-Liquid Extraction and Recovery Process

and was filtered the next day using a Number 2 Whatman Filter paper, a Buchner funnel, and a vacuum filtering flask. The volume of filtrate obtained and subsequently used for feedstock was 925 ml. Each run except Number 12 used 92.5 ml of this filtrate. Run Number 12 was made using 80 ml of filtrate.

One major difference in these five runs was the amount of acid added to the feedstock before any extractions were made. (See Table D-2.) Feedstock in Run Number 7 was acidified to pH 3.54 using 21.65 ml of 1:1 H_2SO_4 with considerable evolution of CO_2 gas. After CO_2 evolution stopped, 6.25 ml of 1:1 NH_4OH was added to bring the pH up to 4.43 to promote greater copper extraction. Six extraction steps were performed (see Figure D-3)* using 100 ml of about 1 molar Naphthenic Acid E (27.5 g) in kerosene and recycling the naphthenic acid after stripping.

Nine stripping steps were performed yielding nine enriched stripping liquors (see Table D-3). Sample 7R1A showed high copper and no nickel and the raffinate showed no copper with moderate to high nickel, but intermediate extraction samples contained various mixtures of the two. Better separation is desirable.

Run 8 feedstock, from the same filtered leach liquor as Run 7, was made beginning at a pH of 8.95 with no acid added. Considerable gas, presumably CO_2, was evolved during extraction operations, but little or none during stripping. This suggests the naphthenic acid was reacting with the ammonium carbonate, producing CO_2. The pH of the raffinate was 8.26 and it contained no copper or nickel, so both were totally extracted. Fifty milliliters of about 1 molar Naphthenic Acid E were used in each of the six extraction steps, with no recycling. This smaller quantity was chosen to try to improve selective stripping since selective extraction, requiring precise pH adjustment, was not used. Attempts to obtain selective stripping from the enriched organic fractions were generally unsuccessful (see Table D-3). None of the enriched stripping liquors was high in either copper or nickel with only a trace or none of the other.

Run 9 was made using 92.5 milliliters of the same leach filtrate as Runs 7 and 8, but with the addition of 5.0 ml of 1:1 H_2SO_4 before any extractions were performed. Considerable gas, presumably CO_2, was evolved both then and during extraction steps. Two 100-milliliter fractions of 1 molar Naphthenic Acid E were used for extractions and were recycled alternately. Examination of the enriched stripping liquors from Run 9 (see Table D-4) shows that the raffinate was totally depleted of copper and nickel. Sample 9RB3 was moderate to

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* This figure illustrates an actual run, showing each step. Subsequent runs followed similar patterns and figures for them have not been included in this report.

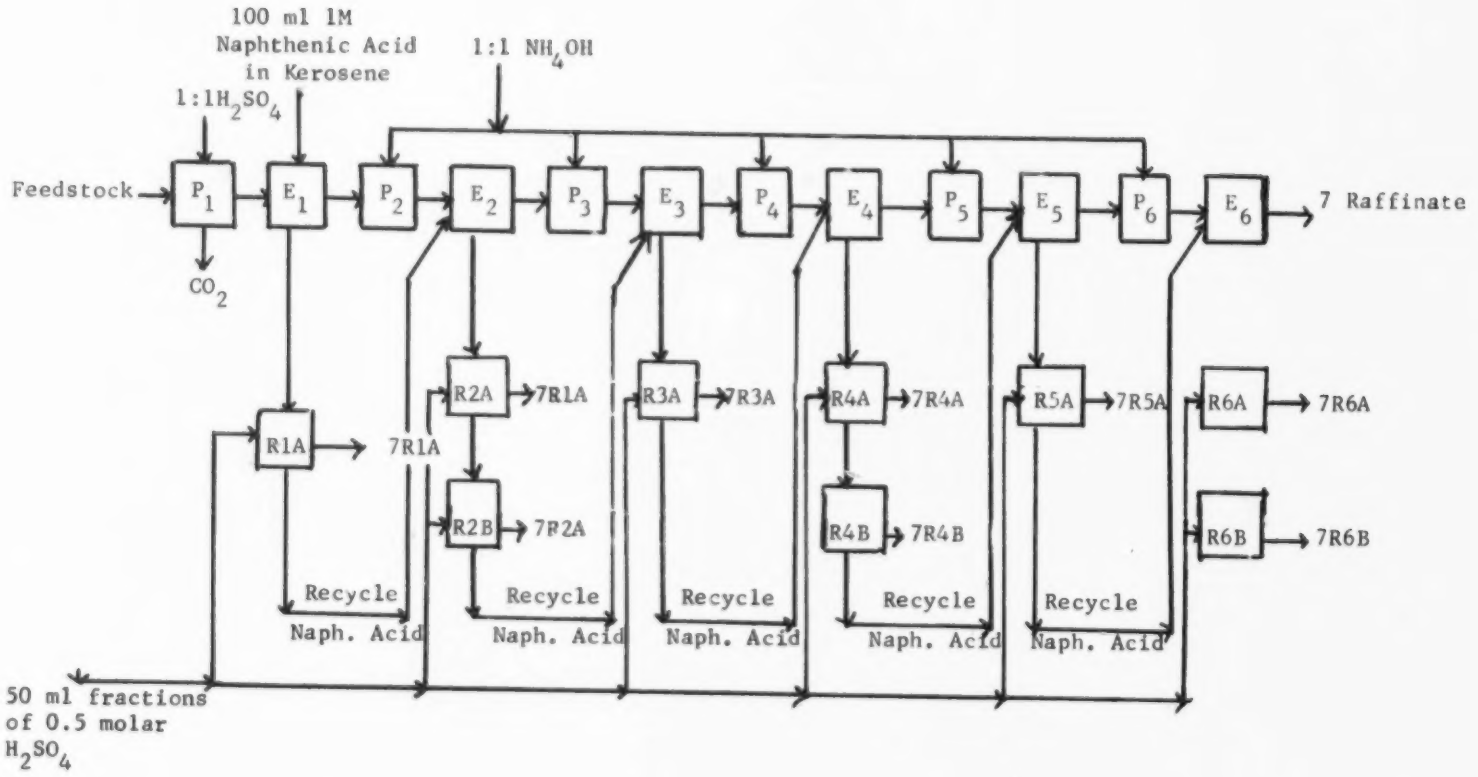

FIGURE D-3. Run 7 Flow Chart

Table D-3. STRIPPING LIQUOR ANALYSES

Sample Number	Nickel Estimate	Copper Estimate	pH Measurement	Quantity of Precipitate[a]
16R1A	Trace-low	Very high	0.73	Much
16R1B	None-trace	Low	0.53	None
16R2A	None	None	6.53	None
16R2B	Very high	Trace	5.62	Much
16R2C	Very high	Trace	0.55	Some
16R2D	Low	None	0.43	None
16R2E	None	None	0.44	None
16 raffinate	Low	None	6.67	None
17R1A	None	Very high	0.71	Much
17R1B	None	Low-moderate	0.46	None
17R2A	Moderate	None-trace	0.55	None
17R3A	None	None	6.70	None
17R3B	None	None	6.24	None
17R3C	Very high	Trace	1.10	Much
17R3D	Moderate-high	None	0.52	None
17R3E	None	None	0.48	None
17 raffinate	Moderate	None	7.20	None
0.5(M) H_2SO_4	None	None	0.42[b]	None

(a) In a few samples, some precipitate formed after several hours.

(b) Recheck of pH of acid and measured 0.42. Earlier measurements averaged 0.53.

high in nickel with only a trace of copper and Sample 9R3B was high in copper with only a trace of nickel. However, Samples 9R1B and 9R2B were moderate to high in both. Since 9R3A and 9R3B were both from the third extraction, they demonstrate that under some circumstances, selective stripping appears to be possible, but more information is needed.

Run 10 is the same as Run 9 except that 10.0 ml of 1:1 H_2SO_4 was added to 92.5 ml ammonium carbonate leach filtrate to make the feedstock. Also the fifth extraction was eliminated since the resulting stripping liquor in Run 9 (9R5A) was low in both nickel and copper. Two 100-ml fractions of about 1 molar Naphthenic Acid E were used and recycled alternately as in Run 9. None of the enriched stripping liquors was high in copper with only a trace or no nickel (see Table D-4), but two samples, 10R1C and 10R2A, were high in nickel with very little or no copper. Again, several samples contained both. Also, it should be noted that Sample 8R1A, 8R2A, 9R1A, 9R2A, and 10R1A show little or no copper and relatively little nickel, although the pH for each stripping liquor is above 7.0, indicating that the sulfuric acid has been exchanged for something since the 0.5 molar H_2SO_4 used in all the stripping operations shows a pH of about 0.53. The material extracted in these samples has not as yet been identified.

Run 11 was made using 95 ml of filtrate from a sulfuric acid leach of Company A dried sludge. The acid leach was made using 1.00 liter of 1:1 H_2SO_4 (by volume) and 100 g of Company A dried sludge. This was stirred for 2 hours at 150 F, allowed to cool and settle, and filtered through a fritted-glass Buchner funnel. The total filtrate was 950 ml. The only problem was that of considerable froth formation during initial mixing of acid and sludge, but the froth was broken by overnight settling, prior to heating.

The 95 ml of acid leach filtrate used in Run 11 was first raised to a pH of 1.7 by adding $Ca(OH)_2$ and filtering. The considerable mass of precipitate required several rinses to recover the soluble metal values. This dilute filtrate and rinse was concentrated by evaporation under vacuum. The concentrated liquor was diluted to 95 ml and the pH found to be 1.71. Sixteen consecutive extractions were performed using two 100-ml batches of about 1 molar Naphthenic Acid E, alternately, and 26 stripping steps were performed (see Table D-4). Samples 11R4A through 11R7B contained nearly all the copper recovered and relatively little of the nickel. Samples 11R8A through 11R16A contained most of the nickel and almost no copper. The total amount of these is presumably greater than in previous runs since the feedstock probably contained about twice as much of nickel and copper feedstock as for the other runs described. Nearly all of the copper and nickel was extracted from the feedstock as shown by the fact that the raffinate showed no copper

Table D-4. ROUGH QUANTITATIVE COMPARISON OF ENRICHED STRIPPING LIQUORS

Sample Number	pH[(a)] of Partly Extracted Enriched Stripping Feedstock		Liquor		
	Before Extraction	After Extraction	pH	Cu	Ni
7R1A	4.43	4.90	0.70	High	None
7R2A	5.03	3.08	0.66	Moderate	Trace
7R2B			0.61	None	Trace
7R3A	5.03	3.32	0.57	Low-mod.	None
7R4A	5.39	4.41	0.59	Moderate	None
7R4B	--	--	0.56	None	Trace
7R5A	5.71	4.83	0.56	Low	Moderate
7R6A	6.95	5.81	0.53	None	Moderate
7R6B	--	--	0.53	None	Low
7 raffinate	5.81	--	--	(None)	(Low-mod.)
8R1A	8.95	N.M.	7.89	Trace	Low
8R1B	--	--	0.92	None	Low
8R1C	--	--	0.70	None	Low
8R2A	N.M.	N.M.	7.53	Trace	Trace
8R2B	--	--	0.74	Moderate	Low
8R2C	--	--	0.70	None	Trace
8R3A	N.M.	N.M.	4.60	High	Low-mod.
8R3B	--	--	0.57	Moderate	None
8R3C	--	--	0.69	None	Trace
8R4A	N.M.	N.M.	1.65	Low-mod.	Low-mod.
8R4B	--	--	0.71	None	Low
8R5A	N.M.	N.M.	1.34	Low-mod.	Low-mod.
8R5B	--	--	0.79	None	Trace
8R6A	N.M.	8.26	1.37	Low-mod.	Low-mod.
8 raffinate	8.26	--	--	(None)	(None)
9R1A	8.23	N.M.	7.63	None	Trace
9R1B	--	--	1.18	Mod.-high	Mod.-high
9R1C	--	--	0.61	None	Low
9R2A	N.M.	N.M.	7.13	None	Low
9R2B	--	--	0.63	Mod.-high	Mod.-high
9R2C	--	--	0.62	None	Low-mod.
9R3A	N.M.	N.M.	4.65	Trace	Mod.-high
9R3B	--	--	0.58	High	Trace
9R4A	N.M.	N.M.	1.42	Low	Low
9R5A	N.M.	7.51	1.08	Low	Low
9 raffinate	7.51	--	--	(None)	(None)

Table D-4. ROUGH QUANTITATIVE COMPARISON OF ENRICHED STRIPPING LIQUORS (Continued)

Sample Number	pH[(a)] of Feedstock Before Extraction	pH[(a)] of Feedstock After Extraction	pH[(a)] of Partly Extracted Enriched Stripping Liquor pH	Cu	Ni
10R1A	7.04	N.M.	7.03	None	Moderate
10R1B	--	--	0.81	High	High
10R1C	--	--	0.65	None	High
10R2A	N.M.	N.M.	3.64	Very low	High
10R2B	--	--	0.64	Low-mod.	Low
10R2C	--	--	0.60	Trace	None
10R3A	N.M.	N.M.	1.20	Low-mod.	High
10R3B	--	--	0.63	None	None
10R4A	N.M.	7.55	0.96	None	Low-mod.
10 raffinate	7.55	--	--	(None)	(None)
11R1A	1.71	1.71	0.57	None	Mod.-high
11R1B	--	--	0.60	None	None
11R2A	2.01	2.01	0.53	None	Mod.-high
11R2B	--	--	0.57	None	Trace
11R3A	3.20	3.10	0.56	Low	Mod.-high
11R3B	--	--	0.53	None	None
11R4A	3.82	3.80	0.55	Mod.-high	Low-mod.
11R4B	--	--	0.59	None	None
11R5A	3.50	3.33	0.55	Low-mod.	Low-mod.
11R5B	--	--	0.54	None	None
11R6A	4.18	3.86	0.72	V. High	Trace
11R6B	--	--	0.58	Low	Trace
11R7A	4.81	3.70	0.58	Mod.-high	Low-mod.
11R7B	--	--	0.57	None	Trace
11R8A	4.87	4.28	0.58	Trace	Low-mod.
11R9A	5.65	3.50	0.58	Low-mod.	Trace
11R9B			0.58	None	Trace
11R10A	5.03	4.20	0.61	None	Low-mod.
11R11A	7.35	5.78	0.85	Trace	High
11R11B	--	--	0.59	None	Mod.
11R12A	5.78	4.32	0.61	None	Mod.
11R13A	N.M.	4.80	0.70	Trace	High
11R14A	7.63	5.83	0.83	None	High
11R14B	--	--	0.63	None	Mod.
11R15A	5.83	N.M.	0.74	None	Trace
11R16A	9.23	6.50	0.85	None	High
11 raffinate	6.50	--	--	(None)	(Trace)

Table D-4. ROUGH QUANTITATIVE COMPARISON OF ENRICHED STRIPPING LIQUORS (Continued)

Sample Number	pH[a] of Feedstock Before Extraction	pH[a] of Feedstock After Extraction	pH[a] of Partly Extracted Enriched Stripping Liquor pH	Cu	Ni
12R1A	6.68	N.M.	7.06	Trace	Low-mod.
12R1B	--	--	1.60	V. High	V. High
12R1C	--	--	0.67	Low-mod.	High
12R1D	--	--	0.67	Trace	Low-mod.
12R1E	--	--	0.71	None	None
12R2A	N.M.	7.02	1.01	None	Low-mod.
12 raffinate	7.02	--	--	(None)	(Low)
13R1A	5.27	2.75	0.70	None	Trace
13R2A	5.60	3.58	0.72	None	Low
13R3A	5.72	3.98	0.77	Mod.-High	Trace
13R4A	6.33	3.13	0.72	Mod.-High	None
13R5A	8.02	3.36	1.03	Low-Mod.	Mod.-High
13R6A	8.50	7.02	6.87	None	None
13R6B	--	--	1.37	Trace	High
13R6C	--	--	0.73	None	Trace
13 raffinate	7.02	--	--	(None)	(Low)
14R1A	3.53	3.70	0.75	Low	Low
14R2A	4.96	3.23		High	Trace
14R3A	6.43	5.72	0.78	Mod.	Low-Mod.
14R3B	--	--	0.70	Trace	Trace
14R4A	7.95	3.60	1.02	Low-mod.	V. High
14R4B	--	--	0.78	Trace	Mod.-High
14R5A	9.63	7.23	6.97	None	None
14R5B	--	--	6.39	None	Low
14R5C	--	--	1.18	Low	High
14R5D	--	--	0.71	None	Mod.
14 raffinate	7.23			(None)	(Trace)

(a) N.M. means not measured.

and only a trace of nickel. Problems with precipitation were encountered around pH 5-6 and required filtering after each pH adjustment step after the 7th extraction. The precipitate probably is mostly chromium compounds. A small amount of this precipitate formation was found in the runs on ammonium carbonate leach; also, in even small amounts of precipitate tend to interfere with separation of the aqueous and organic fractions. Run 11 yielded several usable samples, but some improvements in separation may still be desirable.

Runs 13 and 14 were made using alkaline ammonium sulfate leach of Company A dried sludge. This was selected with hopes of recycling the $(NH_4)_2SO_4$ and to reduce process material costs for acids and bases, which, according to Fletcher and Flett, constitute a significant fraction of the total costs involved.

Run 12 was made using only 80 ml of the ammonium carbonate leach filtrate and 12 ml of 1:1 H_2SO_4 (equivalent to using 15.4 ml of acid with 92.5 ml of filtrate). Only two extraction steps were made using 300 ml of about 1.2 molar Naththenic Acid E in kerosene and recycling. This was done to reduce the variables pertaining to selective stripping, with the objective of extracting all the nickel and copper in one fraction of enriched organic phase, then selectively stripping. This was not successful (see Table D-4). None of the enriched stripping liquor samples was high in copper or nickel with only a trace or none of the other. The controlling factors for selective stripping have still not been determined, through pH and stoichiometric balance seem to be important.

For Run 13, 5.0 g of Company A dried sludge was stirred overnight with 80 ml distilled water and about 20-30 grams of $(NH_4)_2SO_4$ with one drop of 1:1 NH_4OH. This was filtered and the filtrate (pH 7.00) was acidified to pH 3.90 using 0.42 ml of 1:1 H_2SO_4. The organic extract was composed of 100 g Naphthenic Acid E diluted to 300 ml with kerosene (about 1.2 molar) which was recycled through a total of six estractions. Eight enriched stripping liquors were produced (see Table D-4) with good separation of nickel and copper in all samples except 13R5A.

Run 14 was similar to Run 13. The leach liquor was produced by stirring overnight 10.0 g of Company A dried sludge with 90 ml distilled water, 50 g ammonium sulfate, 2 g ammonium carbonate, 1 g dibasic ammonium phosphate, and 3 drops of 1:1 NH_4OH. This was filtered and the filtrate diluted to 150 ml. Of this, 100 ml were used in Run 14. The initial pH of 8.20 was reduced to 3.53 using 1.65 ml of 1:1 H_2SO_4. Five extractions were performed with the pH raised between each by addition of 1:1 NH_4OH or $Ca(OH)_2$. The organic phase was composed of 100 g Naphthenic Acid E diluted to 200 ml with kerosene (about 1.8 molar). This higher molarity was chosen to see if phase separation problems and/or viscosity problems would result. They did not, and,

in fact, the separation of organic and aqueous fractions in Run 14 was better than the other runs, but this is probably due more to the apparent total lack of chromium compounds to produce precipitates, more than the change in molarity of maphthenic acid used. The nickel and copper separation obtained was actually not quite so good as in Run 13, since both 14R3A and 14R4A have moderate amounts of both.

Runs 7, 11, 13, and 14 are the best of the series. Each had some problems, but it is anticipated that application of Fletcher and Flett's suggestions from the source previously cited will further improve separations of Cu and Ni. The various leaching liquors used in these four runs support the feasibility of more than one apprcach. The examples of selective stripping, especially in Run 9, suggest this may perhaps be used as a refinement in conjunction with selective extraction, should it be required (after further study to isolate the controlling variables). Numerous samples have been produced that seem amenable to electrowinning of copper and nickel separately. The chromium may be recovered as a precipitated compound in the case of the acid extraction, or recovered from the cake in the case of extraction in ammoniacal systems.

Run 16 feedstock was prepared from a slightly alkaline ammonium sulfate-ammonium hydroxide leach of Company A dried sludge. Two extractions were performed using Naphthenic Acid E in kerosene. The first extraction (for nickel) was adjusted to a pH of 5.4 and the second (for copper) to a pH of 6.7. Table D-3 shows the estimated levels of nickel and copper in the various stripping liquor samples. The two extractions seem to give good separation of nickel and copper. A small amount of nickel was still present in the raffinate.

Run 17 was performed using a feedstock prepared from an acidic ammonium sulfate-sulfuric acid leach of Company A dried solids. Three extractions were made with Naphthenic Acid E in kerosene at final pH values of 5.3, 5.2, and 7.1. Table D-3 shows the results. There is more nickel in the Run 17 raffinate than in that of Run 16 because NH_4OH was used to adjust the pH in Run 17. This verifies the earlier finding that the use of some $Ca(OH)_2$ to adjust pH in Run 6 precipitates calcium sulfate and seems to permit more complete recovery of nickel.

The results of these last two runs indicate that two extractions, one for copper and a second for nickel, are probably adequate for separation and recovery of these two metals from Company A sludge if the pH is carefully selected and adjusted and if the level of ammonium sulfate is not so high that it interferes with the nickel recovery.

APPENDIX E

ECONOMIC STUDIES

In view of all the considerations and physical variables identified in this study, it is clear that a general "sludge treatment process" is beyond consideration at this point. However, to gain some idea of the economics that might be encountered in such a process, estimates were made to determine the capital and operating costs for a small batch type plant. In designing this process, the order of priorities in process selection was:

(1) detoxification of wastes

(2) simplicity of process

(3) the generation of products amenable to consumption in current metallurgical processes and waste products exhibiting the maximum practical chemical stability.

The plant design and cost estimates were based on batch operation, using the following design basis:

Plant Capacity: 100 lb dry solids/12-hour day/batch

Daily Sludge Feed:

3,330	lb total (3 percent solids)
3,230	lb water
100	lb solids
5	lb Cu
0.3	lb Ni
10	lb Cr
1	lb Fe
0.6	lb Zn
10	lb Ca

A flowsheet of the sludge-treatment process is shown in Figure E-1. A sludge feed (3 percent solids) is preconcentrated by filtration to a solids concentration of 15 percent. The concentrated sludge is then dried in a pan dryer to 41 percent solids. The latter concentration was arrived by assuming that acid leaching is to be carried out with 30 gallons of 20 percent sulfuric acid on 100 lb of dry solids.

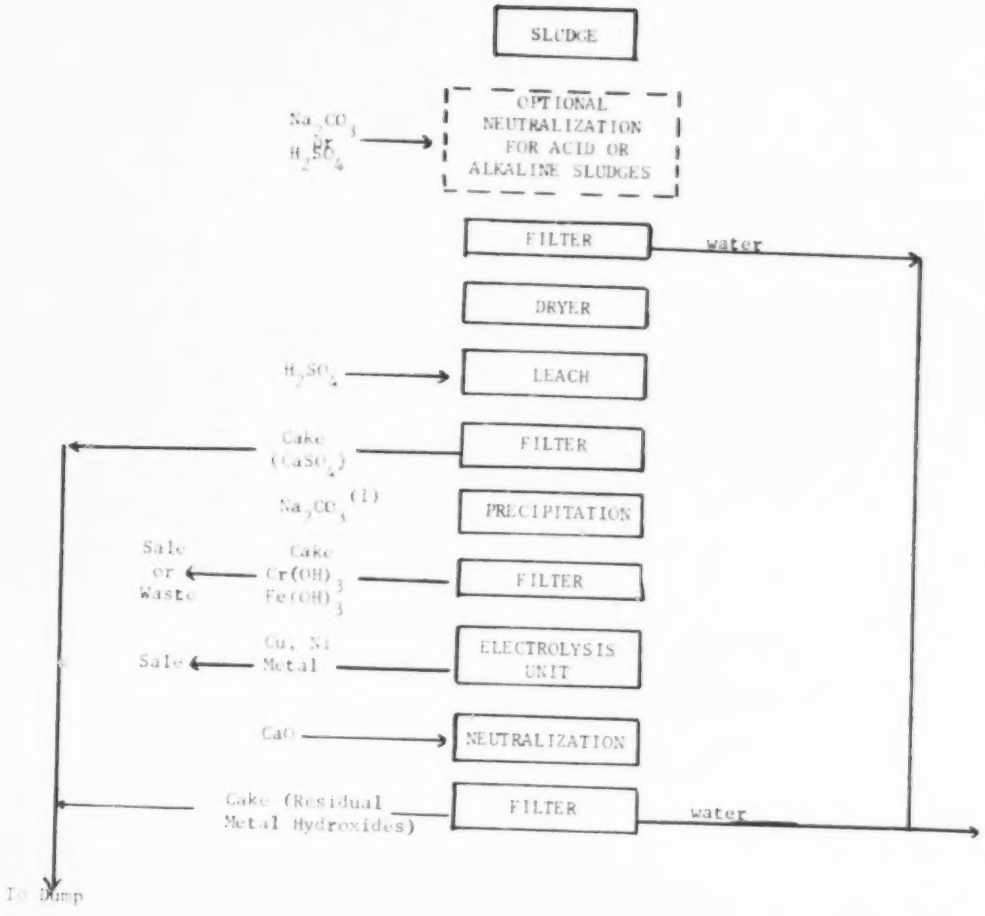

Figure E-1. Flowsheet of proposed sludge treatment pilot process

(1) The efficiency of this separation of iron and chromium from copper and nickel remains to be tested. On carbonate solutions it is easily possible to separate chromium from Fe^{++} and Ni. Data indicate that in a carefully controlled system of carbonate precipitation it might be possible to effect a reasonably good separation of Fe^{+++} from copper. Fe^{+++} is reported to precipitate at near pH 2.5; copper at pH 5 to 5.5. The available data on carbonate precipitation does not show the behavior of Cr^{+++}.

In the leaching step, 58 lb of 98 percent sulfuric acid is added to the dried sludge. The quantity of acid is 1.43 times (43 percent excess) the stoichiometric requirement for neutralization of metal hydroxides (excluding Ca) present in the sludge.

The slurry from the leaching step is filtered to remove solids (calcium sulfate). The filtrate is then neutralized with soda ash to pH 3 to precipitate out $Cr(OH)_3$ and $Fe(OH)_3$. The latter oxides are removed by filtration, and the filtrate is fed into an electrolysis unit removal and recovery of metallic copper and nickel.

After electrolysis is completed, lime is added to the electrolysis solution to neutralize the acid formed from electrolysis. Calcium sulfate and zinc hydroxide precipitate out as the result of neutralization. The lime-treated liquor is filtered in the final step of the process to remove the precipitates.

Valuable materials recovered from the process include: 5 lb of Cu, 0.2 lb of Ni, and 20 lb of $Cr(OH)_3$ (mixed with 2 lb of $Fe(OH)_3$).

The batch operation could probably be accomplished over a 12-hour period according to the following time schedule:

Operation	Duration, hr
Drying	2.0
Leaching	1.0
Precipitation	0.3
Electrolysis	4.0
Neutralization	0.2
Filtration	2.0
Materials Handling	1.5
Start-up and Shut-down	1.0
Total	12.0

A list of equipment and estimated costs is given in Table E-1. The total direct plant cost, exclusive of a trailer for mounting the plant, was estimated as about $15,000. Estimates of operating costs are shown in Table E-2. The daily operating cost was estimated to be about $61 per day. The labor cost is the major cost item.

The plant capacity can be doubled to treat 200 lb/day of sludge on dry-solids basis by operating the plant 24 hours a day.

Table E-1. EQUIPMENT COST SUMMARY

Item	Capacity	Number	Purchased[(a)] Cost, Dollars (1972)
Electrolysis Unit	1.3 lb Cu+Ci/hr	1	3,500
Pan Dryer, 304 stainless	50 ft^2, 10 h.p.	1	3,430
Pressure Filter	1 ft^2	1	600
Leaching/Neutralization Tank, rubber lined	100 gal	1	200
Precipitation Tank, rubber-lined	100 gal	1	200
Agitators, 304 stainless	1 h.p.	2	1,280
Pump, magnetic-coupled	13 gpm @ 6' H_2O 1/4 h.p.	1	100
Purchased Equipment Cost (E)			$9,310
Equipment Installation, 40 percent of E			3,720
Piping (hoses), estimate			100
Instrumentation, estimate			2,000
Total Direct Plant Cost			$15,130

(a) Cost data obtained from: (1) Peters, M. S., and Timmerhaus, K. D., "Plant Design and Economics for Chemical Engineers", McGraw-Hill (1968), (2) Laney, L. E., and Forbes, C. A., "Brass Wire Mill Process Changes and Waste Abatement, Recovery and Reuse", Water Pollution Control Research Series, 12010 DPF 11/71 (1971).

Table E-2. OPERATING COST SUMMARY

Basis: 200 days/year Operation		Daily Cost, dollars/day
Materials		
H_2SO_4, 98% @ 1.7c/lb		0.99
Na_2CO_3 @ 2.5c/lb		0.46
CaO @ 1.0c/lb		0.05
Utilities		
Electricity @ 1c/kwhr		0.16
Steam @ 80c/1000 lb		0.34
Operating Labor @ $5.00/hr		60.00
Maintenance	5 percent of plant cost	3.79
Plant Overhead	30 percent of operating labor plus maintenance	11.94
Depreciation	10 percent of plant cost	7.57
	Total Daily Operating Cost	$85.30

APPENDIX F

BIBLIOGRAPHY

(1) A State-of-the-Art Review of Metal-Finishing Waste Treatment, prepared by Battelle-Columbus Laboratories, for the FWQA and the Metal Finishers' Foundation, November, 1968.

(2) Selected Water Resources Abstracts, Water Resources Scientific Information Center, Office of Water Resources Research, U. S. Department of Interior.

(3) Pollution Abstracts, 6811 La Jolla Blvd., La Jolla, California 92037.

(4) Water Pollution Abstracts, Dept. of the Environment, Her Majesty's Stationery Office, London.

(5) Grune, W. N. Plating and Cyanide Wastes. J. Water Pollution Control Federation, 43:1024, 1971. (Note: This is a yearly feature in the journal.)

(6) Foulke, D. Gardner. Bibliobraphy Metal-Finishing Wastes. Plating. 57:289, 1970.

(7) Kirk-Othmer, Encyclopedia of Chemical Technology, John Wiley & Sons, 1963, 2nd Edition, 22 vols.

(8) Mellor, J. W. A Comprehensive Treatise on Inorganic and Theoretical Chemistry. (London). Longmans Green & Co., Ltd., 1927. 16 vols.

(9) Friend, J. Newton, Editor. A Testbook of Inorganic Chemistry. (London) Charles Griffin & Co., Ltd., 1927. 11 vols.

(10) Gmelins Handbook der Anorganischem Chemie Verlag Chemie, G.M.B.H. (Gmelins Handbook of Inorganic Chemistry, Published by Chemie Corporation). (Berlin) 8th Edition (Still being published).

(11) Linke, William F. Weidell's Solubilities of Inorganic and Metal Organic Compounds. ACS (Washington, D.C.). 1958. 2nd Edition.

(12) Brasted, Robert C. Comprehensive Inorganic Chemistry. D. Van Nostrand, 1961. 11 vols. (Vol. VIII).

(13) Ephram, Fritz. Inorganic Chemistry. Interscience, 1946. 4th Edition Revised.

(14) Sidgwick, N. V. The Chemical Elements and Their Compounds. (Oxford) 1950. 2 vols.

(15) Cotton & Wilkinson. Advanced Inorganic Chemistry. Interscience, 1962.

(16) McAlpine and Soule. Prescott and Johnson Qualitative Chemical Analysis. D. Van Nostrand, 1933.

(17) Latimer and Hildebrand. Reference Book of Inorganic Chemistry. MacMillan, 1951. 3rd Edition.

(18) Mantell, C. L. Industrial Electrochemistry. McGraw-Hill, 1950. 3rd Edition.

(19) Hampel, Clifford A., Editor. The Encyclopedia of Electrochemistry. Reinhold, 1964.

(20) Lowenheim, Fred A., Editor. Modern Electroplating. John Wiley & Sons, 1963. 2nd Edition.

(21) Allmand, H. J. and H. J. T. Ellingham. The Principles of Applied Electrochemistry. Longmans, Green & Co., 1924.

(22) Glasstone, S. Electrolytic Oxidation and Reduction. D. Van Nostrand Co., 1936.

(23) Sand, Henry J. S. Electrochemistry and Electrochemical Analysis. Blackee & Son Ltd., 1941. Vols. I, II and III.

(24) Perry, Robert H., Cecil H. Chilton and Sidney D. Kirkpatrick. Chemical Engineers Handbook. McGraw Hill, 1963. 4th Edition.

(25) Pepperl, H. Incineration of Electroplating Sludges by Means of A Fusion Cone. (In German - Translation on file at Battelle-Columbus Laboratories). Brennst.-Warme-Kraft. 16:399, 1964.

(26) Rehm, F. and S. R. Nietz. Critical Study of Effluent Sludge Disposal Through Low Temperature Incineration. (In German - Translation on file at Battelle-Columbus Laboratories.) Galvanotechnik. 56:462, 1965.

(27) Weiner, Robert F. Acute Problems in Effluent Treatment. Plating. 54:1354, 1967.

(28) Niemetz, W. Disposal of Industrial Sludges. (Presented at the 4th International Congress of the International Research Group on Refuse Disposal (Basel). Schweiz. Z. fur Hydrologie. June 2-5, 1969.) 31:425, 1969.

(29) McGrath, J. J. Treatment of Brass Mill Effluents at Anaconda Toronto Plant. (Presented at the 16th Ontario Ind. Waste Conf., June 15-18, 1969.) 82 p.

(30) Jones, J. L. Electrolytic Recovery of Copper and Sulfuric Acid from Copper Mill Pickling Solutions. Trans. Amer. Electrochem. Soc. 32: 229, 1917.

(31) Whistance, D. J. and E. C. Mantle. Effluent Treatment in the Copper and Copper Alloy Industries. The British Non-Ferrous Metals Research Assn. January, 1965.

(32) Sierp, F. Electrolytische Verfahren, Handbuch der Metallbeizerei (Nichteisenmetalle) (Electrolytic Methods. Handbook of Metal Pickling (Non-Ferrous Metals). Verlag-Chemie (Published by Chemie Corporation). 1951. 100 p. (In German)

(33) Boer, P. Die Ruckgewinnung von Kupfer aus Beizbadern (The Recovery of Copper from Pickling Bath). Metall. 14:1107, 1960. (In German).

(34) Keetman, E. Modern Pickling and Yellow Pickling Baths. Wire and Wire Products. 34:1085, 1959.

(35) Anon. Recovery of Copper and Sulfuric Acid from Pickling Baths. Electroplating. 5:227, 1952.

(36) Anon. Copper Recovery from Pickling Solutions. Metal Industry. 81:370, 1952.

(37) Muller, Richard L. Pollution in the Non-Ferrous Metals Industry-Metal Plating and Electroplating Industries. Waste Disposal Problems in Selected Industries. Edited by John E. Ullmann, Hofstra University Yearbook of Business, Series 6, Vol. 1, 1969.

(38) Wise, William S. The Industrial Waste Problem-IV Brass, Copper, and Electroplating Wastes. Sewage Works J. 20:96, 1948.

(39) Wise, William S. and B. F. Dodge. Industrial Wastes--Brass and Copper Industry. Ind. Eng. Chem. 39:63?, 1947.

(40) McKee, Ralph H. and S. T. Leo. A Continuous Process for Electrolytic Regeneration of Chromic Acid. J. of Industrial and Eng. Chem. 12:16, 1920.

(41) Mitter, G. C. and S. G. Dighe. J. Sci. Ind. Res (India). 2:11, 1943.

(54) Zakarias, M. J. and M. J. Cahalan. Solvent Extraction for Metal Recovery. Trans. Inst. Min. Met. 75:C245, 1966.

(55) Fletcher, A. W. and J. C. Wilson. Naphthenic Acid as a Liquid-Liquid Extraction Reagent for Metals. Trans. Institution of Mining and Metallurgy. 70:355, 1960-61.

(56) Fletcher, A. W. and K. D. Hester. A New Approach to Copper-Nickel Ore Processing. Trans. Soc. Mining Engrs. 229:282, 1964.

(57) Fletcher, A. W. and D. S. Flett. Carboxylic Acids as Reagents for the Solvent Extraction of Metals. Proc. of the Int. Conf. on Solvent Extraction Chemistry of Metals, Edited by McKay, H. A. C., et al., CRC Press, Cleveland, Ohio, September 27-30, 1965.

(58) Fletcher, A. W., et al. Separation of Zinc and Cadmium by Solvent Extraction. Advances on Extractive Metallurgy, Proc. of Symp. by Institution of Mining and Metallurgy (London), Elsevier Publishing Company, April 17-20, 1967.

(59) Baggott, E. R. et al. Recovery of Valuable Metals from Nickel-Cobalt Alloy Scrap. Mineral Processing and Extractive Metallurgy. Proc. of Ninth Commonwealth Mining and Metallurgical Congress. Edited by M. J. Jones. 1969, Vol. 3.

(60) Fletcher, A. W. Metal Extraction from Waste Materials. Chemistry and Industry. 1971. p. 776.

(42) Barnard, Paul G., et al. Recovery of Metallurgical Values from Industrial Wastes. (Presented at Proceedings of the Second Mineral Waste Utilization Symposium, U. S. Bureau of Mines and IIT Research Institute. Chicago, March 18-19, 1970.)

(43) George, L. C. and Andrew A. Cochran. Recovery of Metals from Electroplating Wastes by the Waste-Plus-Waste Method. Bureau of Mines Solid Waste Research Program, Technical Progress Report 27. August, 1970.

(44) George, L. C., et al. The Waste-Plus-Waste Method for Recovering Metals from Electroplating Wastes. (Presented at the A.E.S. Waste Treatment Conference, Post Junior College, Waterbury, Conn. May 21-22, 1974.)

(45) Potter, G. M. Recovery of Nonferrous and Precious Metals from Electrical and Electronic Scrap. (Presented at the Effective Technology and Research for Scrap Metal Recycling Symposium, conducted by NASMI and the U. S. Department of Interior, Bureau of Mines, Washington, D.C. January 7, 1971.)

(46) Brooks, P.T., et al. Chemical Reclaiming of Superalloy Scrap. Bureau of Mines RI 7316. November, 1969.

(47) Brooks, P.T., et al. Processing of Superalloy Scrap. J. Metals. 22:25, 1970.

(47a) Anon. New Recovery Process Can Yield Both Electrolytic Nickel and Copper. Engineering and Mining J. January, 1971. 94 p.

(48) Van Arsdale, George D., Editor. Hydrometallurgy of Metals. McGraw Hill, 1953. 1st Edition. Cementation, p. 188; Leaching, pp. 11-29 and 70-102.

(49) Burkin, A. R. The Chemistry of Hydrometallurgical Processes. E. & F. N. SPON, Ltd. (London), 1966.

(50) Habashi, Fathi. Principles of Extractive Metallurgy - Vol. 2. Hydrometallurgy. Gordon and Breach, 1969. pp. 227-245.

(51) Smithson, G. R., Jr. et al. Liquid-Liquid Extraction of Nonferrous Metals-Review of the Art. J. of Metals. 18:1037, 1966.

(52) Habashi, Fathi. Principles of Extractive Metallurgy-Vol. 2. Hydrometallurgy. Gordon and Breach, 1969. Chap. 17, Solvent Extraction.

(53) Green, H. Separations Using Solvent Extraction. Metallurgia. 70:143, 1964.